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PHYSICS

SOME THEORETICAL ASPECTS OF THE BIOLOGICAL APPLICATIONS OF PHYSICS OF DISPERSE SYSTEMS

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Abstract

A review of the author's recent theoretical work on the properties of small liquid drops and more generally of systems with very large specific surface, is given. When such a system interacts chemically with the surrounding, in such a way, that the mass of the substances, of which the system is constituted, slowly increases, the system will possess, under very general conditions, properties remarkably similar to those found in living organisms. Thus it is found that such a system may possess a positive rate of growth, when its size exceeds a certain critical one. Below this critical size the rate of growth is negative. Such a system therefore can never be formed spontaneously, although all substances necessary for its formation may be present. Under certain very general conditions such a system will, under the influence of osmotic and other forces, divide into two halves, when reaching a certain size, each half again growing and dividing, and so forth. In many cases the system will possess a very definite geometrical form, which will tend to be restored, when the system is deformed by some external disturbance.

EMINENT biologists, such as Bütschli,[1] L. Rhumbler[2] and others[3] have devoted a great deal of their time to the study of various inorganic models, which imitate to a certain extent some properties exhibited by living organisms. Of course, in working with such models, a biologist is perfectly aware of the fact, that these models show only a certain similarity to the corresponding living organisms. If we take a small oil drop, suspended in water, and approach at two opposite ends of a diameter two small pieces of bicarbonate of soda, the surface tension of the drop is lowered at the corresponding two points. Due to the relative increase of the surface tension at the "equator" of the drop, the latter shrinks in the equatorial plane and eventually divides in two.[4] Although this phenomenon shows certain similarities to the division of a living cell, no biologist of course will ever assume, that in the actual cell

[1] Untersuchungen über mikroskopische Schäume und das Protoplasma. Engelmann, Leipzig, 1892.

[2] Methodik der Nachahmung von Lebensvorgängen durch physikalische Konstellationen. Abderhaldens Handbuch der Biol. Arbeitsmethoden. Abt. 5, Teil 3A, p. 219. Urban and Schwarzenberg, Berlin-Wien 1923.

[3] S. Leduc, Solutions and life. Jerome Alexander's Colloid Chemistry **II**, 59. The Chemical Catalogue Co., New York, 1928. A. L. Herrera, Plasmogeny, ibid. p. 81.

[4] J. Spek, Oberflächenspannungsdifferenzen als eine Ursache der Zellteilung. Arch. Entw. Mech. **44**, 35 (1928).

exactly the same phenomena occur. However the observation of such a "model" justifies the more general assumption, that some kind of variations of the surface tension of the cell, probably of a much more complicated nature, may be responsible for the cell-division. The study of such models becomes especially valuable, if it suggests new experiments with the living organisms or new points of view for their interpretation.

The use of models is not unfamiliar to the physicist. However the physicist uses models in a somewhat different way. Whereas in biology, which is yet an experimental science par excellence, the properties of various models are studied by actually experimenting with such models, the physicist frequently satisfies himself with what is called a "Gedankenexperiment." We speak, or rather we used to speak some ten years ago, of the model of the atom. Lord Kelvin made great efforts in imagining models of the luminiferous ether. Clerk Maxwell was endeavoring to make a mechanical model of the electromagnetic field. And yet no one of them did actually "build" any such models, nor experiment with them. These models were, if we may call them so, "paper and pencil models" Mathematical physics has reached a high degree of perfection, and a physicist has enough confidence in the results of his calculations, that he does not need actually to build a model, and may satisfy himself by investigating mathematically, whether such a model is possible or not. The value of such "paper and pencil" models is not only as great as that of actual "experimental" models, but in certain respects it is even greater. The mathematical method has a greater range of possibilities, than the experimental one, the latter being often limited by purely technical difficulties. It is through the study of models that Maxwell finally arrived at his equations, which are and probably will forever remain one of the cornerstones of physics.

The above discussion naturally leads to the question, why we should not use the "paper and pencil" models in biology also? The use of such models here will be particularly advantageous because of the great complexity of all biological phenomena. The technical difficulties of actually building models and experimenting with them, will be considerably greater than in any purely physical problem. Let us therefore make an attempt at studying such "paper and pencil" models of some biological phenomena but let us always keep in mind, that what we study is but a "model," and that no premature claims at any actual "explanations" of the corresponding biological phenomena are as yet justified.

The models to be discussed now are based on several recent theoretical investigations by the writer, dealing with various properties of small liquid drops, to which references will be given consecutively.

Consider a small drop, of a liquid A, suspended in another liquid, B, the two liquids having the same specific gravity and not mixing or reacting with each other. Under these conditions, the drop will assume a spherical shape, and its shape and size will remain indefinitely without change.

Next let us consider a more general case. Suppose that the liquid B contains in solution several substances, C, D, E, F, and that these substances interact in such a way as to form the substance A, which is, as stated, insoluble in B. So that we may symbolically write.

$$C + D + E + F = A. \tag{1}$$

Under such conditions two things will happen. First, new drops of A will be formed here and there in the liquid B, and, second, those drops which have already been formed, will increase in size. If we now investigate the rate of growth of these drops, we shall find, that it will largely depend on a great number of factors.[5] The substances C, D, E, F may be insoluble in the substance A. In that case, the reaction of formation of A will go on only on the surface of the drop. It will be proportional to the concentrations of C, D, E and F in B and to the surface of the drop. The latter being proportional to the 2/3 power of its mass M, we shall have

$$\frac{dM}{dt} = a n_C n_D n_E n_F M^{2/3} \tag{2}$$

where n_C, n_D, n_E, n_F, are the concentrations of the corresponding substances.

Or else the substances C, D, E, F may themselves be soluble in A. In that case they will diffuse from outside into the drop, and the reaction (1) will take place in the whole volume of the drop. However the rate of change of the mass of the drop will not necessarily be proportional to its volume. For the concentrations of the substances C, D, E, F inside the drop will be smaller than outside of it, and these concentrations will themselves be functions of the radius of the drop.

As a matter of illustration let us consider a case of only one "food-substance." We have then instead of (1) a simpler reaction

$$C \rightarrow A \tag{3}$$

which may consist either in a polymerization of C or else in a splitting of C into smaller molecules. Let the concentration of C in B be n_0. If the rate of diffusion of C in A is very large its concentrations inside of the drop will be uniform. If furthermore we limit ourselves to the case, that the rate of growth of the drop is very small, we may with sufficient approximation determine the concentration of C inside of the drop by assuming that the amount of C diffused per second through the surface of the drop from outside is equal to the amount of C transformed per unit time into A inside of the drop.[6] The amount of C diffusing into the drop from outside is equal to

$$4\pi r_0^2 h(n_0 - n) \tag{4}$$

where r_0 is the radius of the drop, n the concentration of C inside the drop and h a constant. The amount of C transformed per second into A is

$$\frac{4}{3}\pi r_0^3 qn \tag{5}$$

[5] N. Raschevsky, Über Gleichgewichte und Reaktionen in Systemen mit sehr grosser spezifischer Oberfläche. Zeits. f. Physik **53,** 107 (1929).

[6] N. Raschevsky, Zur Theorie der spontanen Teilung von microskopischen Tropfen II, Zeits. f. Physik **48,** 513 (1928).

where q is another constant. Equating (4) and (5) we obtain[7,8]

$$n = \frac{hn_0}{h + \frac{1}{3}r_0 q}. \tag{6}$$

Assuming further that the rate of formation of A is proportional to the total amount of C present in the drop, and that C forms only a very dilute solution in A, so that only A practically contributes to the mass of the drop, we shall find that the rate of change of the mass M is now given by[7]

$$\frac{dM}{dt} = \frac{aM}{1 + bM^{1/3}} \tag{7}$$

a and b being constants.

Now let us somewhat generalize our model, by assuming that the substance A undergoes a solution in B at the surface of the drop. Or else we may consider the case, that a substance G is dissolved in B, which, though insoluble in A, reacts with A, giving a product, soluble in B. In both cases the substance A will undergo a process of disappearance, which will be proportional to the surface of the drop, or to $M^{2/3}$. For the total rate of change of M we now find instead of (7) the following expression[7,8]:

$$\frac{dM}{dt} = \frac{aM}{1 + bM^{2/3}} - cM^{2/3}. \tag{8}$$

If we plot dM/dt against M, we obtain a curve, represented on Fig. 1. For $M < M_0 = c^3/(a-bc)^3$ the rate of growth is *negative*. Only for sufficiently large drops this rate of growth becomes positive. The physical reason for this is

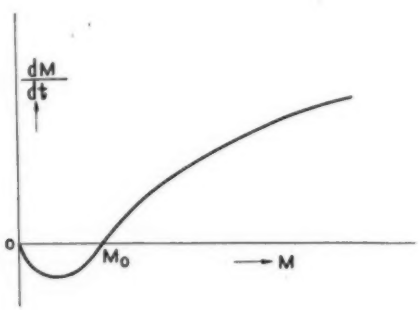

Fig. 1.

simple. The smaller the drop, the larger its specific surface. The process of formation of A is essentially a volume effect, that of disappearance of A—a surface effect. For very small drops the latter prevails, for larger ones the former.

[7] N. Raschevsky, Über durch Diffusion und Auflösung verursachte Wachstumserscheinungen in kleinen Tropfen. Zeits. f. Physik **59**, 558 (1930).

[8] N. Raschevsky, Physical Aspects of Cellular Growth and Multiplication. Protoplasma **13**, (1931).

The conclusions to be drawn from this state of affairs are very interesting. It follows, that although all substances, necessary for the formation of A may be present, and that there is nothing to inhibit the reaction which leads to that formation, no drop of A can be formed spontaneously out of the solution. For such a spontaneous formation presupposes that the drop begins to grow from a very small size, consisting at first only of a few molecules of A. But such a small drop will not grow at all, but will dissolve. Only if a drop of A with a mass larger than the critical mass M_0 is brought from outside into the solution, will it grow further.

Of course we arrived at the Eq. (8) by making a number of rather specialized assumptions. But it may be shown, that this behavior of small growing drops is independent of many of these special assumptions, which we used, as said above, only as a matter of illustration. We may consider the case, that the diffusion coefficient of C in A is sufficiently small. In that case the concentration of C in the drop will not be uniform. It will be larger at the surface and decrease towards the center. [6,8] In such a case the plot of dM/dt against M gives a curve like the one represented in Fig. 2. Again the rate of growth is negative for $M < M_0$, but it is also negative for $M > M_1$. The drop

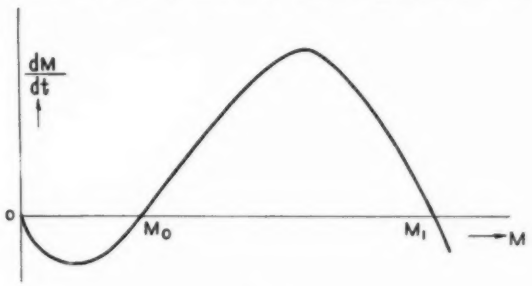

Fig. 2.

cannot be formed spontaneously but it also cannot grow above a limiting size M_1. The reason for such a behavior is this: the larger the drop, the steeper will be the concentration gradient of C at its surface. For very large drops the inside of it is practically free of C, and the formation of A goes on only in a thin layer at the surface. It becomes also proportional to the surface of the drop, and for a proper choice of the constants, it will be balanced out by the process of solution. It is rather interesting to remark, that in this case if we integrate the differential equation for M and plot the M–t curve we obtain an S-shaped curve. It has been found by several biologists, that the actual growth curves of organisms either have a similar S shape, or else they consist of several such S-shaped curves. T. B. Robertson[9] has thought of interpreting this circumstance by assuming that the growth of living substance is due to an autocatalytic reaction. We see, however, that similar growth curves may be due to purely physical reasons and have nothing whatsoever to do with the chemical nature of the reactions involved.

[9] The Chemical Basis of Growth and Senescence. J. B. Lippincott Company, Philadelphia and London, 1923.

We may generalize our model still further by considering the case, that as a result of the reaction between the substances C, D, E etc., not only the substance A is formed, but also other substances, which are soluble in A and B. In this case we shall have instead of (1) an equation of such a kind

$$C + D + E + F = A + G + H + \cdots . \tag{9}$$

The substances G and H will be formed in the drop, and will diffuse from it into the surrounding liquid B. If their rates of diffusion in A are large, the concentration of each of them will be uniform throughout the volume of the drop. But, similarly to the case represented by Eq. (6), these concentrations will be determined at any moment by the instantaneous size of the drop, provided the rate of increase of this size is very small. If, however, the rates of

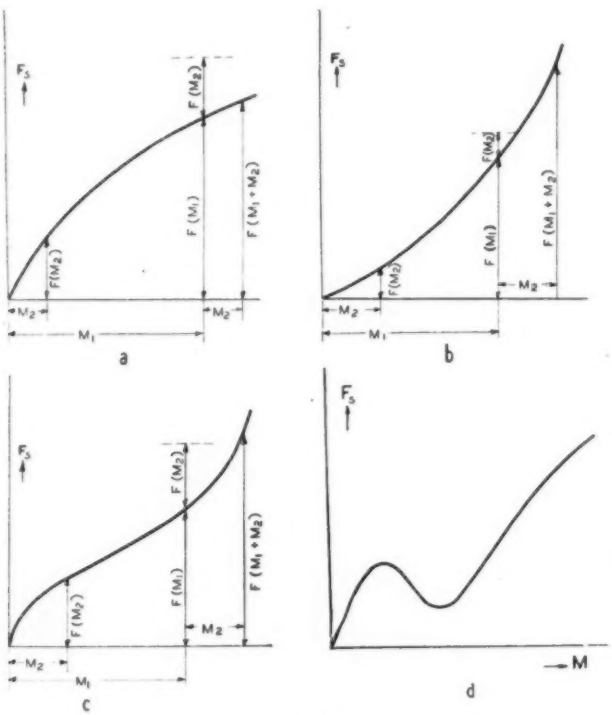

Fig. 3.

diffusion of G and H in A are small, their concentrations in the drop will not be uniform. They will be larger at the center, and drop towards the periphery. But again, for slow growing drops the distribution of concentrations of all substances in the drop is determined by the instantaneous radius of the latter.[6,8]

We may generalize our model still further, by assuming that some of the "by-products" of the reaction (9), for instance G, are not soluble either in A or B, or soluble only in one of them. In this case we shall be led to consider drops, which consist of several distinct phases.[5] For the present we shall restrict ourselves however to simple, single-phase drops.

Let us now investigate the possible fate of such a growing drop. As we have seen, it consists of one substance A, in which are dissolved several "foodstuffs" and "by-products," the concentrations of these dissolved substances varying with the size of the drop. But since the surface tension of a liquid is always changed by the addition of various other soluble substances, all the above means that the surface tension of such a growing drop will also vary, as the size of the drop varies. If the surface tension were constant, the total surface energy of the drop which is equal to $4\pi r_0^2$ would vary as the $\frac{2}{3}$ power of its mass (curve a, Fig. 3). However, since this will not be the case, the surface energy may vary in some other way, as represented on Fig. 3. Suppose the surface tension increases very rapidly with increasing size of the drop, so that for the surface energy F we get a curve like $3b$. Suppose we divide in some way such a drop in two parts, which are either equal or unequal. The total surface of the two smaller drops will be larger than the surface of the original larger drop, but surface tension having decreased more rapidly than the increase of the surface, the total surface energy of the two parts will be smaller than the total surface energy of the whole, as seen from Fig. $3b$. But

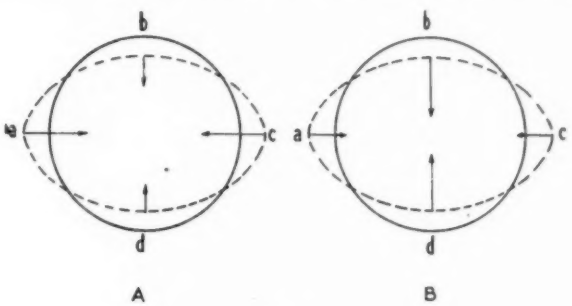

Fig. 4.

this means, that when such a drop divides in two, energy is liberated. Therefore such a division will take place spontaneously. The consideration of Fig. 4 will make clear the mechanism of such a spontaneous division.

As long as the drop is perfectly spherical, the distribution of the concentrations of all substances inside it possesses a spherical symmetry. The concentration of any substance is the same at all points of the surface, and the same holds therefore for the surface tension. Suppose that through some external disturbance, the shape of the drop has undergone a slight deformation, so that it is now a stretched ellipsoid. In an ordinary drop, with constant surface tension, this will result in a decrease of the capillary pressure at points b and d Fig. $4A$, and in an increase at a and c because of the change in the curvature of the surface. A distribution of capillary pressure, such as shown on Fig. $4A$, will result, and this will tend to restore the spherical shape of the drop. In case however of a drop, in which diffusion processes of the above mentioned nature take place, things will be different. When the drop is deformed into an ellipsoid, the concentrations of the various substances contained therein will no longer be the same at all points of the surface. For

those substances which diffuse *into* the drop (C, D, E, F) the concentration will become larger at a and c, smaller at b and d (Fig. 4B). For those substances which diffuse from the drop, (G, H), the opposite will be true.[10,6,8] As a result of this, the surface tension will also vary from point to point along the surface of the ellipsoid. And, as will happen in a drop, which corresponds to Fig. 3b, it may happen that at points b and d the surface tension will increase more than the curvature will have decreased .The capillary pressure, which is the product of the surface tension by the mean curvature, will therefore become larger at b and d (Fig. 4B) than at a and c. Such a distribution of capillary pressure will tend to make the drop shrink along the equatorial plane and divide in two.[4]

Returning now to Fig. 3b, we see, that however small the drop will be, it always will continue to divide spontaneously into smaller ones. Such a drop therefore cannot exist at all, as it will gradually disappear. Whereas a drop which corresponds to Fig. 3a, will never spontaneously divide, and may grow to any size. If however the surface tension will increase first slowly with the size of the drop, then more rapidly, we shall obtain a curve, shown in Fig. 3c. In that case we see, that the drop will divide spontaneously only after it has reached a certain size, not below that size. A similar thing will happen, if the surface tension will have a minimum for a certain size of the drop (Fig. 3d).[6] The answer to the question, as to whether the drop will divide into equal or unequal parts, will depend on the exact shape of the F-M curve.

We thus see that a drop of the nature considered above will under not too specialized conditions divide in two, after reaching a certain size. The two "daughter-drops" will naturally grow further, and each of them, having reached the critical size, will divide again, and so on. As long as we restrict ourselves to drops, which consist only of one substance, and to the case where all the other substances, present in the drop, form only very dilute solutions, the size of the drop will be determined by its mass, and since the distribution of the concentrations of the diffusing substances are determined entirely by its size, the division of all the "generations" of drops will occur at the same "critical size." Two drops of the same size will possess the same rate of growth and be similar in all other respects.

If however the drop consists of several substances A_1, A_2, A_3, insoluble in B, then drops of the same size may possess different masses, depending on the ratios of the relative amounts of A_1, A_2, etc. Unless the rates of formations of all these substances are governed by a single reaction, so that the relative amounts of A_1, A_2, A_3. . . remain constant, the intervals between two consecutive divisions of different "generations" will not be the same, and drop of different generations will not be quite similar.[5,6,8,11]

A spontaneous division of a small growing drop may however be due also

[10] N. Raschevsky, Zur Theorie der spontanen Teilung von mikroskopischen Tropfen. Zeits. f. Physik **46,** 568 (1928).

[11] N. Raschevsky, Uber durch physikalische Struktur hervorgerufene Kettenreaktionen. Zeits. f. Physik **64,** 556 (1930).

to a somewhat different physical cause.[12] Experimental work of the last two decades[13] has established the existence of "two-dimensional" or "surface" phases, consisting of monomolecular layers of substances, absorbed at the surface of a liquid. Hitherto only such cases have been studied, where the surface phase does not interact chemically with the substance, forming the "volume" phase. It is, however, natural to consider the possibility of a reversible reaction between the "surface" and the "volume" phase. The thermodynamical study of such a possibility leads to the conclusion, first suggested by F. G. Donnan[14] and later on worked out mathematically in more detail by the writer,[12, 8] that the surface tension in this case will depend on the total area of the absorbing surface, for a constant volume. It may happen that, with increasing area, the surface tension will decrease more rapidly, so that in spite of the increased surface, the total surface energy decreases. In this case an increase of the surface will take place spontaneously. Instead of assuming a spherical shape, which corresponds to a minimum surface, a liquid drop, which has such a monomolecular layer at its surface, will spontaneously stretch, and assume various nonspherical shapes. The contradiction of this behavior with the laws of capillary pressure is only an apparent one, as a more detailed mathematical investigation shows.[8, 12] For a given volume V there is a definite value of the area of the surface, for which the surface energy has a minimum. For this value of the surface the capillary pressure is at all points zero. If this surface S is larger than

$$(36\pi)^{1/3}V^{2/3}$$

and remains single-connected, then the shape of the drop cannot be spherical because for a sphere

$$S = (36\pi)^{1/3}V^{2/3}.$$

But since the shape in this case may be varied in an infinite number of ways, without altering the surface area, the shape of the drop will remain indetermined. The drop may acquire any shape whatsoever. Under other conditions, the spontaneous increase of the surface may occur not by mere stretching of the drop, but by its division into two or several smaller drops.[12]

The above considerations of liquid drops which possess a nonspherical shape, brings us to the general problem of forms, which may be assumed by liquid drops, suspended in another liquid, so as to be free of the action of gravity. Let us return again to the diffusion processes in the drop, as considered above. Suppose that the drop has a nonspherical shape. In that case, as we have seen on page 150, the concentrations of the diffusing substances will vary from point to point along the surface of the drop, and therefore also the

[12] N. Raschevsky, Uber Gleichgewichte in Systemen, welche flächenhaft verteilte Phasen enthalten, etc. Zeits. f. Physik **51,** 571 (1928).

[13] Lord Rayleigh, Phil. Mag. **5,** 321 (1890) Scient. Pap. **3,** 383 T. Langmuir. Journ. Am. Chem. Soc. **39,** 1848 (1917). W. D. Harkins, ibid. 354 (1917). N. K. Adam. Proc Roy. Soc. **A99,** 336 (1921) **101,** 452 and 516, (1922) **103,** 676 and 687 (1923). R. Delaplace. Journ. d. Physique (6) **9,** 111 (1928). For other references c.f. reference 12.

[14] The Theory of Capillarity and Colloid Solutions. Zeits. f. physik. Chem. **46,** 197 (1903).

surface tension will not be the same at all points. This results in general in a nonuniform distribution of the capillary pressure along the surface, (Fig. 4) and therefore such a drop will not be stable. It either assumes a spherical shape, or else divides into two smaller spherical drops.

It is however conceivable that for some shapes of the drop the distribution of the concentrations, or in other words, the distribution of the surface tension along the surface, will be such that although the surface tension varies from point to point, its product with the mean curvature of the surface at the corresponding point has the same value for all points of the surface. The capillary pressure being now uniform over the whole surface, the drop will be in equilibrium for that particular shape.

The mathematical problem of determining such equilibrium shapes for given diffusing substances is rather complicated, and has not yet been solved. That however such nonspherical figures of equilibria are possible can be shown in a much simpler way. Thus for instance,[15] if we consider a drop, which has the shape shown in Fig. 5*a*, and assume, that a substance diffuses

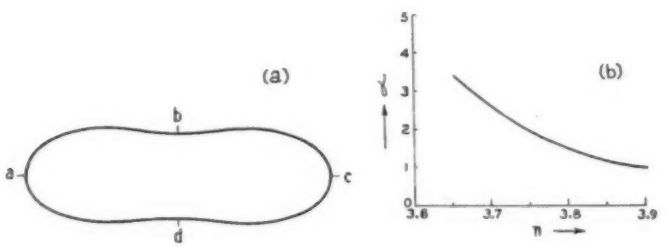

Fig. 5.

from outside into it, and undergoes there a transformation, at a rate proportional to its concentration, we find by graphical integration, that for a definite choice of the constants involved, the distribution of the concentration along a meridianal line, *ab*, will be such, that it will be largest at *a* and gradually drop down as we proceed towards the point *b* on the line *ab*.

In order that the product of the surface tension with the mean curvature should be constant along the line *ab*, the relation between γ and the concentration must be represented by a curve 5*b*. But this is a rather typical curve of any capillary archive substance. Inversely, we must conclude, that whenever a substance with such a γ-n curve diffuses into a drop, the shape 5*a* is a shape of equilibrium. Things become of course much more complicated, when we consider cases of several diffusing substances.

Another shape of equilibrium exists in every case, namely the sphere. This shape may be either the more stable or the less stable one, depending on whether the total surface energy is smaller or larger than for the nonspherical shape. It is also important to remark, that such nonspherical shapes of equilibria may exist only as long as the processes of diffusion and chemical

[15] N. Raschevsky, Zur Theorie der bei Diffusion in kleinen Tropfen entstehenden Gleichgewichtsfiguren. Zeits. f. Physik **56**, 297 (1929).

transformations persist in the drop. If these processes stop, if the drop becomes a purely static system, it will necessarily round up to a sphere. Without suggesting this as an explanation we venture to remark, that some protozoa, who during their life have a nonspherical shape, in spite of their protoplasm being liquid, assume a spherical shape after death.

Glancing back on the several properties which our theoretical drops possess, we see, that first of all they show what may be called quite generally "metabolism." Two processes, that of formation of the substance, of which the drop is composed, "assimilation," and that of destruction of this substance, or "dissimilation," go on all the time in the drop.

No drop can be formed spontaneously. But since every drop, after reaching a critical size divides in two, new drops may be formed through fission of the older ones, and their number may increase indefinitely, as long as the necessary "food substances" are available. Removal of these food-substances does not merely stop the growth of the drops, but causes them to undergo a process of solution. A growing drop may sometimes possess a nonspherical form, which it will reconstitute, if the latter is disturbed due to an external force. But as soon as growth, or rather the physicochemical processes which cause it, are suspended, the drop will acquire a spherical shape. Our drop constitutes indeed a "model" of a simplest living organism.

In concluding we wish to emphasize once more, that there is still a great distance between such a model and an actual theoretical explanation of various phenomena in living cells. But we believe that the study of the former is the first step towards the latter. We wish to repeat here what we said in one of our earliest publications on this subject:[10] We are sure that if the possibility of application of physics to biological problems is admitted at all, and thus a certain competency is granted in these problems to the physicist, the investigation of this domain is to proceed by first studying rather simple, intentionally idealized cases. Later on gradually more complicated cases should be studied. Only after we make it clear theoretically, what phenomena are at all conceivable in this field, and what may be their *possible* causes, shall the experiment decide, which of all these conceivable causes are actually present in living nature.

The author wishes to express his sincere thanks to Professor Davenport Hooker, who kindly looked over the manuscript of this paper and made several valuable comments.

THE LIMITATIONS AND ADAPTABILITY OF ULTRAMICROSCOPES TO THE STUDY OF COLLOID SYSTEMS

By L. V. Foster

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Abstract

Ultramicroscopes are of two distinctly different types. The best known is the cardioid ultramicroscope in which the illuminating portion produces a hollow cone of large angular aperture with its apex at the object. The observing system is a microscope consisting of a high aperture objective of angular aperture slightly less than that of the hollow cone and a high power eyepiece. The other is the slit ultramicroscope. The illumination system in the slit ultramicroscope is perpendicular to the observing system. Both systems are of high numerical aperture, but no direct light can enter the observation system. Details of construction of both types of ultramicroscopes and their sensitiveness of adjustment are discussed. Expressions of their limitations in colloid microscopy are given.

A POWERFUL beam of light directed through a suspension becomes visible by virtue of light scattered by the particles which make up the suspension. This was observed by Tyndall and is known as the "Tyndall effect." Zsigmondy realized that particles in a very finely divided state existed in colloidal solutions and went to Siedentopf with the problem of making them visible. The first solution of the problem was the cardioid ultramicroscope. With this instrument, ultramicroscopic particles could be seen in liquids. Colloids, however, may exist in solids and Siedentopf and Zsigmondy working together solved the problem of making visible colloids in solids with the slit ultramicroscope.

The purpose of this paper is to describe the functions of these two kinds of ultramicroscopes. The first will be that in which the illumination and observation beams of light are concentric. These have been classed generally as dark field condensers. Many forms have been made by the various optical manufacturers, but only the parabolic dark field condenser, attributed to Wenham in 1856 and the cardioid condenser invented by Dr. Siedentopf in 1910 will be discussed here. In the second form, the illumination and observation beams of light are 90° apart. This ultramicroscope was first described by Drs. Siedentopf and Zsigmondy in the Annalen der Physik in 1903.

In the ordinary bright field microscope, Abbe has shown that resolution cannot be carried beyond a quarter micron. The particles dealt with in ultramicroscopy are only a fraction of a wave-length of light and are too small to be resolvable. The underlying principle of the visibility of ultramicroscopic particles is that when illuminated by a strong beam of light they diffract some of this light in all directions and become luminous. If enough of this

diffracted light is picked up by the eye or an optical instrument the particles will appear to be small disks of light. They may be seen as individual disks of light provided they are separated by distances resolvable by a microscope.

The examination of materials for ultramicroscopic particles has been of great help to the chemist. Colloidal solutions and colloidal solids may be brought to the microscope and their state of subdivision may be analyzed. It is possible to detect conglomerates and to see Brownian movement. Coagulation may be determined by counting particles at different times after adding the coagulant. Solutions may be treated chemically while observations are being made, and the results observed. The speed of Brownian motion may be used as a crude measure of the size of the particles.

Ultramicroscopic particles may be differentiated from simple fluorescence. Solutions in which a Tyndall beam is seen may be due either to fluorescence or diffraction. The use of an analyzer will extinguish the beam if it is due to

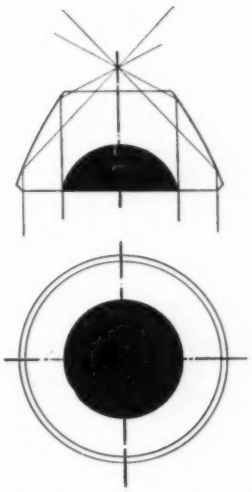

Fig. 1. Parabolic dark field condenser.

diffraction from actual particles while no position of orientation of the analyzer will extinguish a fluorescent beam.

The two forms of ultramicroscopes already mentioned make it possible to recognize these submicroscopic particles because a very concentrated beam of light is directed through the medium containing the particles but none of this direct concentrated light is allowed to enter the microscope and consequently reach the eye. When this concentrated beam of light impinges on these particles they become visible by the cone of rays which they diffract. A further consideration of this will be taken up after having described the manner in which this concentrated beam of light is made to fall on these particles.

Fig. 1 shows the parabolic dark field condenser. The reflecting surface is a paraboloid of revolution and the center is stopped by an opaque disk. Parallel light entering the annular ring is reflected at the parabolic surface and comes

to focus in the plane of an object which may be mounted on a glass slide of about 1.5 mm thickness. Only light within the hollow cone illuminates the object. Particles in the focus of the light diffract light into the unilluminated solid cone where the microscope objective can be placed to examine them.

The paraboloid of revolution would be an ideal surface for concentrating light in a point were it not for the fact that it is not free from coma, i.e., it is not aplanatic. This causes considerable loss of light concentration.

The cardioid ultramicroscope gets its name from the geometrical curve which is produced by the trace of a point on the circumference of a circle as it rolls on another circle of equal radius. This curve generated is a cardioid, heart shape, the equation being $R=r\ (1+\cos\alpha)$ where r is a constant. Dr. H. Siedentopf[1] described the cardioid condenser in the Zeitschrift fur wissenschaftliche Mikroskopie, 1910. The cardioid curve is the caustic curve resulting from rays reflected from a circular surface when a luminous point is on the circumference of the reflecting circle.

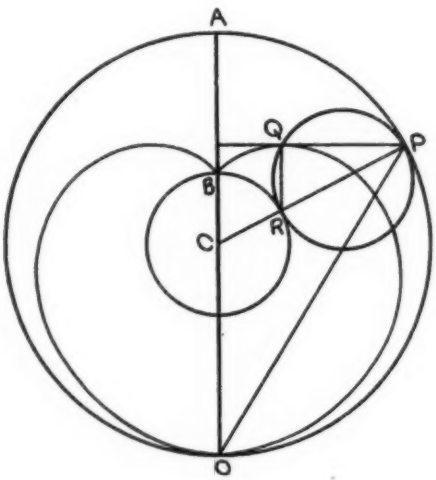

Fig. 2.

Fig. 2 shows O is the luminous point on the circle APO. PQR is a circle of radius equal to the radius of the circle BR. As PQR rolls on BR, Q will describe the caustic BQO which is a cardioid and it can be proven that any ray starting at O and reflected from the circle APO will be tangent to this curve

If this curve, Fig. 3, be combined with a circle of radius RC, and its center located in a definite position, all the rays incident parallel to the axis will, after reflections at the convex surface of the circle, and at the concave surface of the cardioid, pass through the cusp of the cardioid. The center of the circle will be below the cusp of the cardioid by an amount equal to $\frac{1}{2}$ its radius. This combination of cardioid and circle fulfills the Abbe sine condition namely $f=h/\sin\alpha$ since $\sin\alpha=h/r$ and the cardioid condenser is aplanatic.

[1] Dr. H. Siedentopf, Zeits. f. wissenschaftliche Mikroskopie, 1910.

The actual form which the application of these curves takes in the construction of the cardioid is shown in Fig. 4. *A* is a planoparallel glass plate cemented to *B* which has a concave spherical surface and a portion of a cardioid of revolution *C* about the vertical axis. Both surfaces *S* and *C* are silvered. *D* is a planoparallel glass with an annular ring aperture through which parallel light enters and is brought to focus at the object *O*.

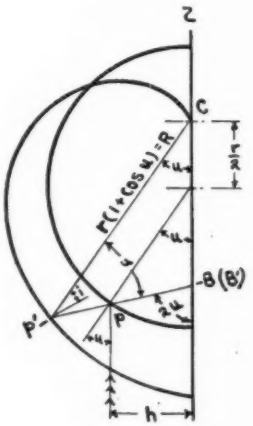

Fig. 3.

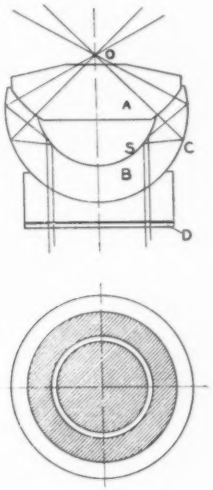

Fig. 4.

The cardioid condenser is best used with a very strong arc lamp focused to direct parallel light into the condenser so that the maximum concentration of light will reach *O*. Since this concentration is so great, ordinary glass slides and cover glasses are not practical. They are not free enough from visible defects and they cannot be cleaned sufficiently well to avoid foreign objects ruining the visibility of ultramicroscopic particles. Fused quartz object slides and fused quartz covers are consequently used. They are entirely free from bubbles, are perfectly isotropic and can be heated in a flame to drive off all dirt after being chemically cleaned.

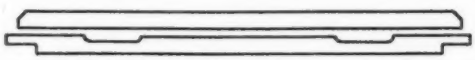

Fig. 5.

Fig. 5. The fused quartz slide is made with a platform surrounded by a moat for catching overflow. The platform is about 2 to 3 microns below the surface of the support for the cover. The cover is made 0.75 mm thick in order to avoid it bending into the cell. Since the ordinary microscope objectives are not designed to work through such thick covers special objectives have to be used. Special apochromatic objectives of 0.85 N.A. are recommended. The apochromatic objective is to be preferred over the achromatic inasmuch as

they will stand a much higher eyepiece magnification than achromatic objectives.

The cardioid ultramicroscope is limited to the examination of liquid colloids. It is impossible to prepare a thin enough section of a solid to be examined in this manner.

In 1903 Siedentopf and Zsigmondy[2] published in Annalen der Physik an article entitled "The Visibility and Determination of Size of Ultramicroscopic Particles with Special Application to Gold Ruby Glass." The ultramicroscope referred to in this article is the slit ultramicroscope in which the object is illuminated by a cone of light 90° to the axis of an observation microscope.

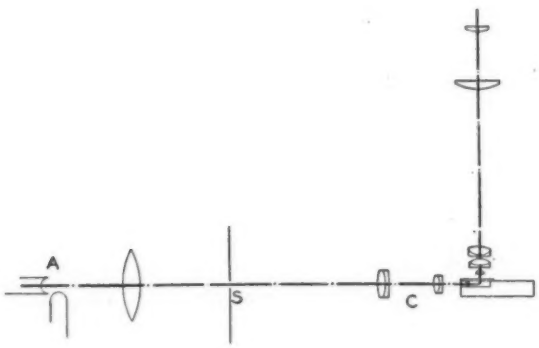

Fig. 6.

Fig. 6. The crater of an arc lamp *A* is focused on a horizontal slit *S* which is imaged by a condenser *C* in the object. The slit is horizontal and only a thin section of the object is illuminated. The observation microscope consists of objective and eyepiece. (As in the case of the paraboloid dark field condenser and the cardioid condenser no direct light from the condenser enters the observation microscope.) Colloids in liquids, solids or gases may be examined in this manner. The solid must have at least one surface fairly well polished and another surface making an angle of about 90° with it for examination. The polished surface is the one through which the observing microscope is focused. The light enters the other surface. Gases may be enclosed in a chamber similar to the liquid chamber.

The question of "how large are the smallest particles visible by ultramicroscopic means?" has been solved by Siedentopf by a consideration of the amount of radiation from the particles and the limit of sensitiveness of the eye. The first of these is dependent upon specific intensity of radiation, and of the radiating surface and the solid angle at which the radiation is emitted from the surface. Siedentopf states that the limit of the smallest size of particle visible with the ultramicroscope is forty square millionths of a millimeter which corresponds to a circle of radius about 4/1,000,000 millimeter.

[2] Dr. H. Siedentopf, Ann. d. Physik, 1903.

The diameter is 0.008μ. Svedberg[3] gives a formulae for the radius of an ultramicroscope particle $r = (3M/4n\pi\rho)^{1/3}$. All the particles in a known volume of the sol are counted and M is the total mass (determined analytically) in this volume, n the number of particles and ρ the density. It is assumed here that the density of the ultramicroscopic particles is the same as the mass material and that the particles are spheres. The form of these particles can be observed by twinkling, double refraction and anisotropy. Twinkling particles are dissymmetric. Dissymmetry is also observed by measuring the double refraction of the sol induced by a magnetic or electric field.

With the slit ultramicroscope and an arc lamp the limit of size of particles discernible is said to be between 5 and 15 mμ.

[3] Dr. Th. Svedberg, Colloid Symposium Monograph, 1923.

CONDUCTIVITIES OF LOW ORDER IN HYDROCARBONS AND TRANSFORMER OIL

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(Received June 10, 1931)

Abstract

A method is described for removing moisture, air and soluble and suspended matter from oils and hydrocarbons in preparation for measurements of the d.c. conductivities and the power factors. The method at the same time provides for cleaning of the measuring cell and insures that no contamination occurs while measurements are being made. Normal decane, transformer oil and dimethyl octane were studied. In each case, d.c. conductivities in the lower range of 10^{-18} ohm^{-1} cm^{-1} were obtained, suggesting that if individual hydrocarbons have characteristic d.c. conductivities they must be of the order 10^{-19} or lower. In each substance the power factor was reduced to $\cos\theta = 0.0004$ at room temperatures. A normal temperature-power factor function was found for the purified transformer oil. Near saturation was observed at the early stages of purification. Then, as purification proceeded, there was approach to Ohm's law, and finally approach to saturation again. It is pointed out that saturation at the early stages is the unexpected and unexplained feature. Some time-current curves and volt-ampere characteristics bearing on the phenomenon of electrical cleaning are included.

Introduction

THE true electrical characteristics of highly insulating liquids such as hydrocarbons and the complex mixture of those which constitute the insulating oils obtained from petroleum are as yet unknown. The values obtained for dielectric strength and power loss and particularly the conductivities under d.c. stress are remarkably dependent on the methods and extent of purification. Von Schweidler[1] studied six substances of high grade. Without attempts at extreme purification and without particular precautions against the entrance of air and moisture, he obtained the following results for the conductivities in ohms^{-1} cm^{-1}: toluene, 6×10^{-13}; benzene, 2×10^{-13}; distilled benzene, 4×10^{-14}; petroleum, 3×10^{-13}; benzine, 3×10^{-15} and hexane, 4×10^{-16}. Jaffé,[2] on the other hand, by repeated distillation until no further change took place, but measuring in an open vessel exposed to air and atmospheric moisture obtained these results: petroleum ether, $<10^{-18}$; carbon tetrachloride, 1.3×10^{-17}; carbon bisulphide, 8×10^{-17} and benzene 4.4×10^{-17}. These results of Von Schweidler and Jaffé were obtained at low stresses where Ohm's law is obeyed, and at room temperature.

Most of our knowledge of the conductivities of insulating oils is naturally confined to those observed at high stresses where Ohm's law does not hold.

[1] E. von Schweidler, Ann. d. Physik **4,** 307 (1901); **5,** 583 (1901).
[2] G. Jaffé, Ann. d. Physik **28,** 326 (1909).

The transformer oil in general use about this laboratory in connection with the testing of cables has a conductivity of about 2×10^{-14} ohm^{-1} cm^{-1} at a stress of 40,000 volts/cm and at room temperature. A conductivity as low as 3×10^{-16} ohm^{-1} cm^{-1} at a stress of 10,000 volts/cm has been observed in specially prepared small samples.[3] However, Schrader[4] and Nikuradse[5] have made measurements on insulating oils at low stresses within the Ohm's law region. The former obtained conductivities of about 1×10^{-14} and 8×10^{-14} ohm^{-1} cm^{-1} for the two transformer oils that he studied. Nikuradse obtained on a mineral oil purified to an "extreme" degree by filtration, drying and electrical cleaning a conductivity as low as 3×10^{-15} ohm^{-1} cm^{-1}.

It is evident that a study designed to determine the real behavior of hydrocarbons under electrical stress and to establish a possible correlation between such behavior and molecular structure is especially subject to error from various sources. Of course we must be sure of the purity of the material in the sense of organic chemistry. In addition we must be sure that more obvious impurities known to affect dielectric properties such as moisture, air, suspended matter and soluble matter from the measuring apparatus are removed before the measurements are made. It is with the latter phase that this paper is concerned. A method is described for removing these more obvious impurities. The d.c. conductivities and power factors observed in a transformer oil and moderately pure normal decane and 2.7 dimethyl octane are reported. While the limiting d.c. conductivities are believed to be smaller than any heretofore reported, it is not claimed that they are the smallest attainable with the materials and the method employed. Nor is it claimed that they are characteristic of chemically pure normal decane and dimethyl octane. The paper closes with a discussion of the volt-ampere characteristics at various stages of cleaning and some observations related to "electrical cleaning."

The Experimental Scheme

The scheme is designed to achieve three things in one series of operations:

(1) Air is to be removed by the pump while the liquid is evaporating and freezing at very low pressures.

(2) Moisture is to be removed by contact with sodium, the hydrogen evolved being also removed by the pump.

(3) Suspended and soluble matter introduced by the cell is to be removed by repeated flushing with the distillate.

The method is illustrated in Fig. 1 which shows the combination still and and conductivity-power factor cell. The system is all Pyrex glass connected at *P* through flexible copper tubing and through traps to a mercury vapor pump capable of pressures as low as 10^{-6} mm Hg. The electrodes and guard rings are made of steel and are rigidly supported in their proper relative positions by ground Pyrex glass rings. The rings supporting the central high ten-

[3] J. B. Whitehead, in a private communication.

[4] J. E. Schrader, Elect. Journ. **16,** 334 (1919).

[5] A. Nikuradse, Archiv. f. Elektrotechnik **22,** 283 (1929).

sion electrode are fluted on the outside to permit free flow of liquid into the interior of the condenser. The diameter of the high tension electrode is 1.397 cm (0.550 inches) and the internal diameter of the low tension electrode is 1.905 cm (0.750 inches) so that the thickness of dielectric becomes 0.254 cm (0.100 inches). The length of the low tension electrode and, hence, the effective length of the condenser is 10.16 cm (4.00 inches). The cell constant A/l in the relation $\rho = RA/l$ is 208 cm, and the air capacity is 18.4 micromicrofarad. Connections are made through sealed-in tungsten wires.

The still is of the "molecular" type first used by Brönstedt and v. Hevesy[6] for separating the isotopes of mercury and later employed by Washburn[7] and Hibben[8] for separating the chemical constituents of petroleum and for removing dissolved gases from liquids. At the same time the system as a whole realizes the method of Kenrick[9] for obtaining liquids free of suspended particles.

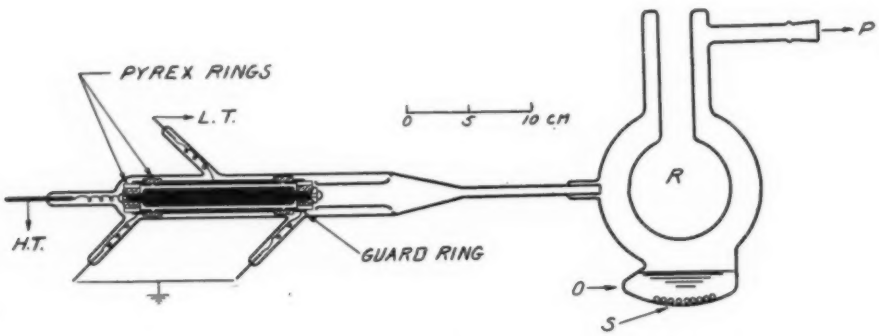

Fig. 1. Combination conductivity—power factor cell and still.

The system is supported with the axis of the cell approximately horizontal. Short lengths of sodium wire, S, are introduced through the side tube and about 75 cm^3 of oil or hydrocarbon, O, are poured in and the pump connection closed. The liquid evaporates at the low pressures maintained by the pump and is frozen on the inner bulb which is kept cold by a refrigerant, R, which may be either a mixture of carbon dioxide snow and ether or liquid air. When the oil or hydrocarbon has been frozen on the inner bulb the system is lifted to another support arranged so that the axis of the cell is vertical. The indentation at the side of the outer bulb prevents the pieces of sodium and any residue that may be left from falling into the cell. The refrigerant is removed and as the liquid melts it drains off into the cell where its conductivity or power factor may be measured. After a set of measurements has been completed the liquid may be returned to the still and the process repeated as often as desired.

[6] J. N. Brönstedt and G. v. Hevesy, Phil. Mag. **43,** 31 (1922).
[7] E. W. Washburn, Bureau of Standards, J. of Research **2,** 476 (1929).
[8] J. H. Hibben, Bureau of Standards, J. of Research **3,** 97 (1929).
[9] F. B. Kenrick, J. Phys. Chem. **26,** 72 (1922).

It was found that 75 cm^3 of normal decane could be distilled and frozen in about one hour with carbon dioxide snow-ether slush as a refrigerant. Liquid air was required when working with dimethyl octane. 75 cm^3 of this substance were distilled and frozen in about 50 minutes. In each case distillation was so rapid that moisture froze on the bottom of the still. The transformer oil proved to be just barely manageable in this still with carbon dioxide snow-ether for refrigeration. On account of the low vapor pressure the oil was heated; never however above 97°C since the sodium did not melt. Perhaps most of the drying of the transformer oil occurred when it was warm. Owing to radiation from the warm oil, oil began to drip off the inner bulb as the oil thickness increased. Being a mixture, the transformer oil also evaporated at a diminishing rate. By gradually lowering the temperature as distillation proceeded, in order to minimize dripping from the inner bulb, it was eventually possible to condense 75 percent of the 75 cm^3 of oil in about 8 hours. This amount was sufficient to cover the high tension electrode of the cell which is all that is necessary. The indentation at the side of the still was deep enough to retain the residue when the still was tipped.

The hydrocarbons were obtained from the Eastman Kodak Company. It was not claimed for them, that they were strictly pure. The boiling point range for the normal decane was stated to be 101 to 103°C at 70 mm pressure and for the dimethyl octane 156 to 158°C at atmospheric pressure.

While sodium was used primarily as a drier it serves also to remove many substances that are known to be or are often assumed to be injurious in dielectrics and which may be present in minute amounts. A partial list of these is perhaps of interest.

(1) Organic and inorganic acids form nonvolatile sodium salts.

(2) Ketones which may condense to enols and then form sodium salts with liberation of hydrogen.

(3) Weak bases such as ammonia or pyridine which would be freed from their salts and, being volatile, may be removed by the pump in spite of the refrigerant.

(4) Alcohols which would form sodium salts.

(5) Sulphur compounds such as mercaptans which form salts that would not decompose in the absence of water.

(6) Unsaturated hydrocarbons which may undergo hydrogenation in the presence of sodium and nascent hydrogen.

(7) Aldehydes which may be polymerized with liberation of water, which is in turn acted upon by sodium.

The Electrical Measurements

The source of direct current was a set of dry batteries giving a range from 1.5 to 2160 volts. The currents were measured with a Compton quadrant electrometer by the rate-of-charge method. A wide range of current sensitiveness was attained by varying the electrometer sensitivity and by the use of a variable precision condenser having a range from 50 to 1500 micromicrofarad. The capacity of the cell, the electrometer and the rather long connec-

tions combined was found to be 117 micromicrofarad. This value was determined with decane in the cell. It was assumed to be the same when working with transformer oil and dimethyl octane.

The power factors were measured with an Atkinson[10] bridge, the source of power being a single phase high tension transformer operating at 60 cycles.

No attempt was made to control the temperature while measuring the d.c. conductivities. The observations were made at room temperatures which varied from 20 to 25°C. Power factor measurements were made on transformer oil at three different temperatures.

Since the system remained evacuated while the measurements were made, the pressures were the vapor pressures plus the hydrostatic pressures of the liquids in the cell. Generally, the surface of the liquid stood 9 cm above the center of the condenser. The mean densities of the three substances studied may be taken to be 0.80 g/cm³. The mean hydrostatic pressures were therefore 5.3 mm Hg.

The D. C. Conductivities

The main results are shown in the volt-ampere characteristics assembled in Fig. 2 and in Tables I, II and III showing the conductivities at a low stress, an intermediate stress, and the highest stress that was employed. Generally, only the former is in the region where Ohm's law is obeyed. These volt-ampere characteristics and conductivities are based on the nearly steady currents observed after a sufficient time interval at each stress in increasing order.

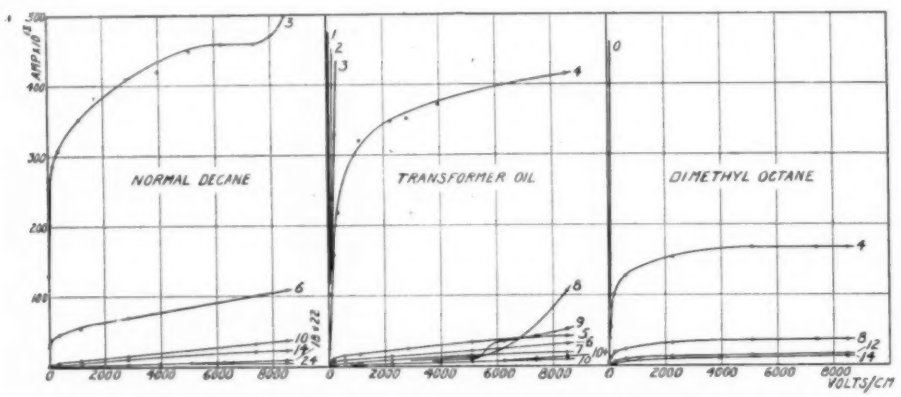

Fig. 2. Volt-ampere characteristics. They are based on the final steady currents. The numbers refer to number of distillations.

Data for normal decane after distillations 1 and 2 are not shown since the electrometer was still being adjusted. The conductivities were high and probably within the range observed in transformer oil after the first three distillations.

A part of the high conductivity in transformer oil after the first distillation is due to the fact that about 2 cm³ of residue spilled over the indentation

[10] R. W. Atkinson, Elect. Journ. **22,** 58 (1925).

TABLE I. *d.c. conductivity of normal decane.*

Number of distillations	Conductivity, ohm^{-1} cm^{-1}, at stress of		
	11.8 volts/cm	1200 volts/cm	8500 volts/cm
3	2.1×10^{-14}	5.7×10^{-16}	1.2×10^{-16}
6	4.7×10^{-15}	8.9×10^{-17}	2.5×10^{-17}
10	1.9×10^{-16}	1.4×10^{-17}	7.7×10^{-18}
14	5.4×10^{-17}	8.0×10^{-18}	5.3×10^{-18}
18	5.4×10^{-18}	2.2×10^{-18}	1.6×10^{-18}
22	5.8×10^{-18}	1.9×10^{-18}	1.7×10^{-18}
24	Not determined	3.7×10^{-18}	1.1×10^{-18}

TABLE II. *d.c. conductivity of transformer oil.*

Number of distillations	Conductivity, ohm^{-1} cm^{-1}, at stress of		
	11.8 volts/cm	1200 volts/cm	8500 volts/cm
1	4.0×10^{-14}	Not determined	Not determined
2	7.4×10^{-15}	Not determined	Not determined
3	5.8×10^{-15}	2.9×10^{-15}	Not determined
4	3.8×10^{-15}	5.3×10^{-16}	9.4×10^{-17}
5	6.9×10^{-16}	2.6×10^{-17}	9.2×10^{-18}
6	3.1×10^{-16}	1.4×10^{-17}	6.9×10^{-18}
7	3.3×10^{-17}	6.1×10^{-18}	4.1×10^{-18}
8	2.3×10^{-17}	4.1×10^{-18}	2.4×10^{-17}
9	1.3×10^{-17}	1.9×10^{-18}	1.1×10^{-17}
10	1.2×10^{-17}	1.6×10^{-18}	1.9×10^{-18}
10+ (from residue)	8.0×10^{-18}	1.6×10^{-18}	2.4×10^{-18}

TABLE III. *d.c. conductivity of dimethyl octane.*

Number of distillations	Conductivity, ohm^{-1} cm^{-1}, at stress of		
	11.8 volts/cm	1200 volts/cm	8500 volts/cm
0	$>7\times10^{-14}$	Not determined	Not determined
4	6.0×10^{-15}	2.2×10^{-16}	3.8×10^{-17}
8	8.2×10^{-16}	4.7×10^{-17}	8.1×10^{-18}
12	1.3×10^{-16}	1.6×10^{-17}	3.5×10^{-18}
14	4.2×10^{-17}	1.1×10^{-17}	3.0×10^{-18}

in the still and ran into the cell. This may have delayed matters and made more distillations and flushings necessary in order to reach the low conductivities shown in curve 10. These are of the order of twice the lowest observed with decane and very likely, could have been reduced still further by continued work.

Up to stresses of 5100 volts/cm the curves 1 to 10 appear in regular decreasing order. After distillations 8 and 9 the conductivities were higher than expected at the higher stresses. The currents were also unsteady. The oil was evidently in some temporary condition since after distillation 10, the curve is normal again and lies under all of the others. Possibly some residue may have splashed over by the drip from the inner bulb while distillation 8 was carried out.

It has been explained that the distillate from transformer oil represented about 75 percent of the oil. Distillate from distillation 10 was left in the cell and more oil was distilled over from the residue until, finally, 96 percent of the oil was in the cell. The conductivities, indicated by 10+, were practically the same as after the tenth distillation. This result makes it highly improbable that "good" fractions were distilled off during the earlier operations, leaving "poor" fractions behind. If there are poor components present in the oil they are a part of the 4 percent left as residue after distillation 10+.

Low conductivities were obtained with dimethyl octane also. It is apparent that the limit was not reached. Work was discontinued after 14 distillations on account of accident to the liquid air container. The results with this substance are of interest chiefly in that they give some hint as to the effective factor in the operations that were carried out. The drying record (contact with sodium) for all three of the substances studied is shown in Table IV. It will be observed that the dimethyl octane was in contact with sodium in the evacuated system for 50 days before any measurements were made. The zero with which the first curve is labelled indicates that no distillation was made. The system was turned over and the liquid allowed to run directly into the cell. The conclusion would seem to be that the really effective factor in the operations is not drying, nor purification as far as that is realized by sodium alone; but that it is elimination of suspended matter in the liquid and the washing out of suspended and soluble matter acquired in the cell.

TABLE IV. *Record of drying time (contact with sodium).*

Normal decane		Transformer oil		Dimethyl octane	
Distillation	Time (days)	Distillation	Time (days)	Distillation	Time (days)
3	5	1	4	0	50
6	11	2	5	4	60
10	14	3	6	8	69
14	19	4	10	12	70
18	24	5	10	14	71
22	29	6	13		
24	34	7	13		
		8	14		
		9	16		
		10	18		
		10+	18		

The three outstanding results of the work which has been described are: (1) the d.c. conductivities can be reduced to the lower range of the order 10^{-18} ohm^{-1} cm^{-1} in normal decane, transformer oil and dimethyl octane; (2) it can be done by the simple operations of high vacuum distillation, drying with sodium, and repeated flushing out of the measuring cell without the use of any chemical processes whatever other than those that may take place during contact with sodium; and (3) if individual pure hydrocarbons have characteristic d.c. conductivities they must be within the order 10^{-19} ohm^{-1} cm^{-1} or lower and would be very difficult to establish.

The Power-Factors

Power factor changes were not followed throughout the series of distillations; measurements being only after the final distillations. At stresses of 29,500 volts/cm (75,000 volts/inch) and at room temperature, the power factors in each case; normal decane, transformer oil and dimethyl octane were: $\cos\theta = 0.0004$. The a.c. conductances calculated by the formula $G = 2\pi fC \cos\theta$ were

$$G = 6.28 \times 60 \times 36 \times 10^{-12} \times 4 \times 10^{-4}$$
$$= 5.4 \times 10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}.$$

It is interesting to compare the initial short time d.c. conductivities with the final d.c. conductivities for evidence of absorption or losses of dipole origin. Pending further work in which it is hoped to measure initial conductivities within 0.001 second after application of stress, they may be taken to be equal to the foregoing a.c. conductances as calculated from the power factors.[11] The ratio of initial to final conductivities is, in order of magnitude, $10^{-12}/10^{-18} = 10^6$. Apparently, this is enormously greater than the ratio, 8, recently observed by Whitehead in a high grade transformer oil designated as B-6. However, if that ratio had been computed on the basis of a final conductivity of the order 1000 times smaller as was observed in this work and if the stress had been twice as high so as to correspond to those used in the present power factor measurements, it would have been 16,000 instead of 8; only 60 times smaller than the present ratio of 10^6. This high ratio emphasizes the conclusion of Whitehead that "even after the most careful purification by the methods mentioned, an initial absorption and a conductivity much greater than the final conductivity remain."

The power factor-temperature function was of the same form in this transformer oil, after 10 distillations, as in ordinary commerical oils. At stresses of 29,500 volts/cm and at temperatures of 25°, 99° and 135°C, the power factors were, respectively, 0.0004, 0.0021 and 0.0046.

Changes in the Volt-Ampere Characteristics

A study of the conductivity Tables I, II and III reveals that the most rapid fall in conductivity occurs at the lowest stress. In other words the volt-ampere characteristics tend to straighten out and approach Ohm's law. This behavior is shown also in Fig. 2 although not very clearly on account of the scales necessary to exhibit the large variations in the conductivities. Fig. 3, in which all of the curves of Fig. 2 appear, is designed to show it more clearly. Each curve is correctly drawn but a different scale is employed for each of them. For example, in the case of normal decane, curve 3 was drawn. Then a scale was chosen for curve 6 so that it would lie just under curve 3, a scale for curve 10 was chosen so that it would lie immediately under curve 6 and so on. However, beyond a certain stage in the "purification" there is departure from

[11] J. B. Whitehead, Conductivity of Insulating Oils, II, Presented at the Winter Convention of the A.I.E.E., New York, Jan. 26–30, 1931.

Ohm's law again and approach to saturation. Saturation was actually achieved in normal decane after the last distillation and there was approach to saturation in transformer oil after distillations 8, 9 and 10. Work on dimethyl octane was discontinued at a stage where the volt-ampere characteristic was still straightening out.

The interesting and at the same time the difficult feature common to the three sets of curves in Fig. 3 is saturation or near saturation at the early stages of purification. We would expect saturation at the end of a series of distillations if all electrolytic impurities have been removed and if ionization due to radioactive influence predominates over any spontaneous ionization of the liquid.[12] And we would expect Ohm's law to hold at all earlier stages if practically all of the conduction is due to electrolytic impurities. It would seem that the appearance of saturation or near saturation at early stages in the present experiments and their frequent appearance in commercial oils is to be regarded as unexpected and as the feature that requires explanation.

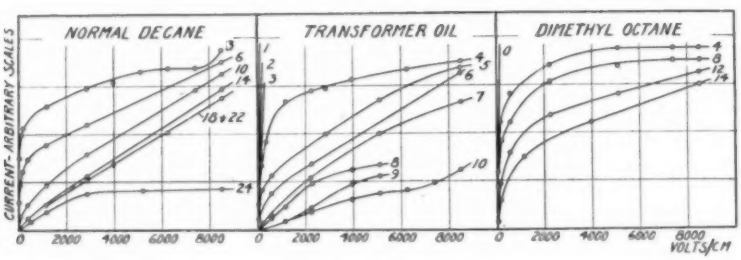

Fig. 3. Volt-ampere characteristics. Same as in Fig. 2 but drawn to arbitrary scales to show more clearly their change in form as the liquids are purified.

The behavior at the earlier stages is the same as that observed by Jaffe[13] in hexane after contamination with small amounts of lead oleate. Near saturation was found and he was led to assume that the rate of dissociation into ions was small compared with the rate with which they disappeared at the electrodes. But, as Baars[14] remarks, one must not forget that it is evidence of polarization; specifically, evidence of the phenomenon of limiting currents as observed in electrolytes.[15]

"Electrical Cleaning"

All three of the substances studied gave evidence of the phenomenon called electrical cleaning. It showed itself not only as a gradual decrease of current with time at a particular stress. It was found that the largest currents were obtained at some intermediate stress when a series of time-current observations were made in succession at increasing stresses. The set of time-current

[12] G. Jaffé, Ann. d. Physik **28,** 326 (1909).

[13] G. Jaffé, Ann. d. Physik **36,** 25 (1911).

[14] E. Baars, Handbuch der Physik, Julius Springer, Berlin, 1928, Band XIII, p. 404.

[15] Reference 14, p. 558.

curves obtained with dimethyl octane after distillation No. 4 as shown in Fig. 4 is illustrative, although it represents a series of observations rather more complex than usual.

A consequence of the behavior shown in Fig. 4 is that volt-ampere char-

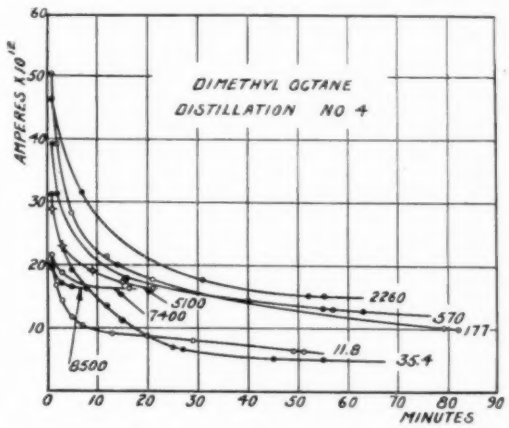

Fig. 4. Time current curves.

acteristics based on currents observed after various times after application of the stress will show maxima and minima for the shorter times. It is only when the characteristics are based on current observations after 30 minutes or more

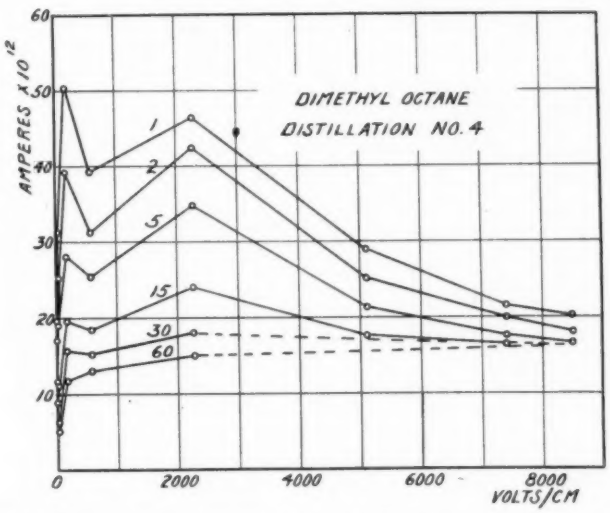

Fig. 5. Volt-ampere characteristics derived from Fig. 4 with various times as parameters. The numbers refer to minutes after applying stress.

that they assume the usual form. The volt-ampere characteristics constructed from Fig. 4 with various times, in minutes, as parameters are shown in Fig. 5. The curve marked 60 in this figure is the same as the curve marked 4 in Fig. 2, for dimethyl octane since that was based on the nearly steady

values of the currents attained after sufficiently long intervals of time. Of course it is not known that the true positions of the maxima in the volt-ampere characteristics based on the shorter time intervals should really be at 177 and 2260 volts/cm since the observations were made at widely spaced voltages. The volt-ampere characteristics in Fig. 5 suggest that two sets of ions contributed to the current in dimethyl octane after distillation No. 4. One set was relatively mobile and reached the electrodes most rapidly at 177 volts/cm. The second set was of a sluggish type and reached the electrodes at the maximum rate at a stress of 2260 volts/cm.

It was only in dimethyl octane that the volt-ampere characteristics based on short time intervals showed two maxima. In normal decane the lone maximum appeared at 35 volts/cm and in transformer oil there was one maximum at 177 volts/cm.

The effect of successive distillation is to make these maxima less and less prominent. In general, near the end of a series of distillations, the time-current curves such as shown in Fig. 4 would lie one under the other in regular order with increasing stress, without any intersections.

Acknowledgments

I am indebted to Mr. R. W. Atkinson, Dr. J. B. Whitehead and Mr. J. G. Niedercorn for criticism and much helpful advice.

A VOLTAGE SELECTIVE NONLINEAR BRIDGE

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(Received July 13, 1931)

Abstract

The important property of the simple series resonance circuit employing resistance, capacitance and an iron core reactor arranged to saturate is the abrupt increase in current at a certain critical voltage. This phenomenon is identified as a quasi-resonant condition, and is compared to resonance in linear circuits. An experimental study is made of a nonlinear bridge circuit comprising two branches of the above type. This bridge is *voltage selective* in such a manner that the load is only energized thru a certain range (of the supply voltage), which may be small. The variation of bridge output voltage (effective) with bridge supply voltage may be critical. In one case it is observed that 1/100 percent change in supply voltage changes the output (load) voltage by 100 percent. The properties of the bridge circuit are applied to the problem of voltage selective relays which permit the control of many circuits by means of a two wire system. For a bridge comprising identical capacitance and inductance units, but dissimilar resistance, a constant voltage characteristic is noted.

(A) The Series Nonlinear Circuit

ELECTRICAL circuits comprising elements of inductance, capacitance or resistance which depend upon the current are usually distinguished by nonlinear volt-ampere characteristics. In particular the series resistance, capacitance, iron core inductance circuit may exhibit the interesting volt-ampere relation of Fig. 1.* The linear region (a) of small current is associated with the unsaturated condition of the iron while the linear region (c) is had for saturation values of the core material. The region (b) of most rapid change in current with voltage is the most significant characteristic condition for the circuit. It is found that for the region (b) the current rises to such maximum value that instantaneously the capacitance and inductance voltages become equal and opposite, resulting in a quasi-resonance state called *nonlinear resonance*.** Nonlinear resonance thus bears an analogy to resonance in linear circuits in that the instantaneous value of the current is resistance limited, the sum of the reactance zero; it differs from the more familiar resonance phenomena in that the resonance conditions exist during only a small portion of each steady state cycle. This remarkable situation for which resonance depends predominantly upon voltage follows fundamentally from the great dependence of impedance upon voltage for reactors of closed core, saturation properties.

The critical voltage for nonlinear resonance or simply the "resonant voltage" varies with frequency in a manner which is approximately linear for

* See bibliography at end of paper.
** Bibliography 11.

small ranges, being greater for higher frequency. It is further found that the resonant voltage does not depend upon capacitance or resistance critically. The most significant single factor in determining the resonant voltage is the nature of the saturation characteristic for the iron. For a given material, however, the critical voltage varies approximately as the number of turns on the core.

The resonant voltage in the nonlinear circuit has an importance analogous to the resonant frequency in linear circuits; it may be determined in any given case for standard magnetic materials by various approximate methods of little merit and negligible accuracy. A purely analytical means of obtaining this quantity with good accuracy is described in a paper now in preparation.

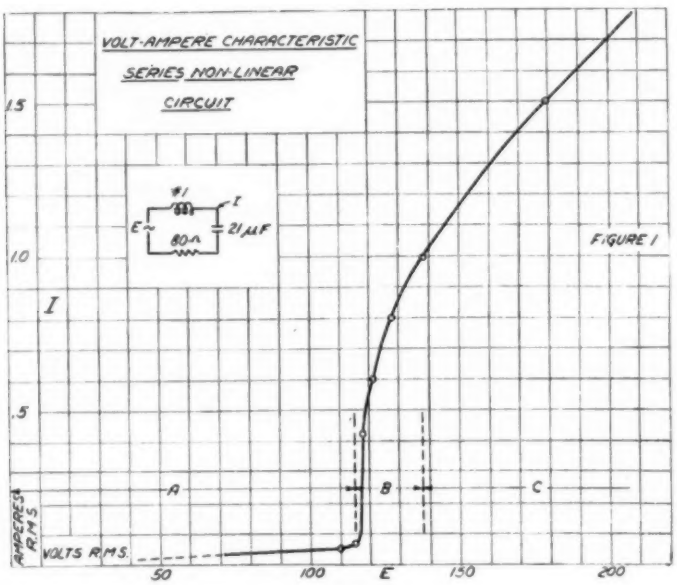

Fig. 1.

(B) The Nonlinear Bridge; Voltage Selectivity

Two series circuits of the type of Fig. 1 may be combined as in Fig. 2 to produce a bridge circuit of remarkable properties. The output voltage of the bridge is the difference voltage E_0 between the two condensers, which have a common connection. Thus it is evident that the voltage E_0 is large only when the two series circuits (1) and (2) of Fig. 2 are in *dissimilar* resonance condition. Hence if both arms comprise indentical elements, the voltage E_0 will remain theoretically zero for all values of the applied voltage E. This condition may be very closely approximated in practice.

Consider the case of dissimilar series branches (1) and (2). Suppose $R_1 = R_2$, $C_1 = C_2$, and let the reactors be identical except in the number of turns, which differ by a small percentage. It is clear that under this condition the two arms of the bridge will have resonant voltages which differ by a small per-

centage. If the output voltage E_0 is measured as a function of the applied voltage E a characteristic of the form of Fig. 3 may be obtained. Thus for values of E between $E=0$ and $E=109$ neither circuit is in a condition of non linear resonance, the condenser voltages are small, and their difference is negligibly small on the scale of this curve. At the value $E=109$ circuit (1) of Fig. 2 has attained its critical or resonant voltage, the current rises rapidly, producing a

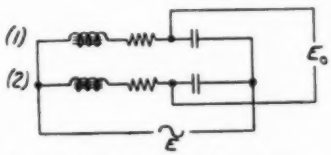

Fig. 2. Nonlinear bridge circuit.

high voltage across the condenser C_1. The condenser difference voltage E_0 becomes very large and remains so until E becomes equal to 111 volts, the critical voltage for branch (2). As soon as both circuits are in nonlinear resonance the voltage E_0 again assumes a low value which is maintained for subsequent increases in E. It will be recognized, of course, that the balance which is

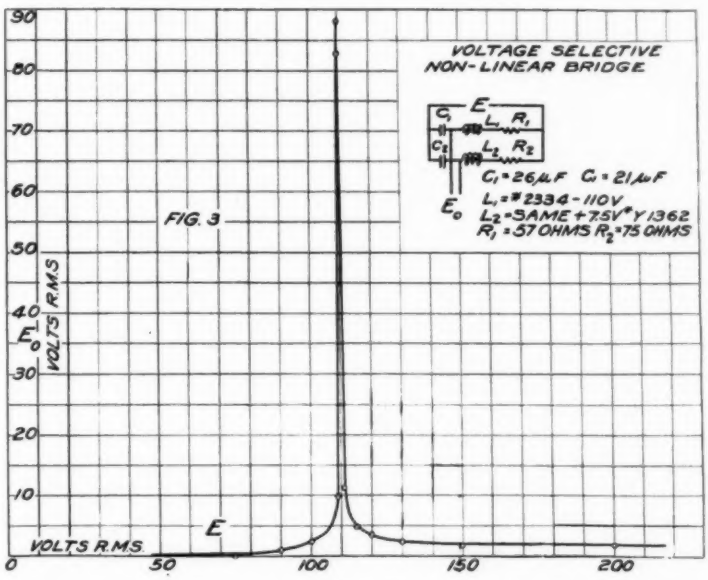

Fig. 3.

obtained in the condenser voltages is between the instantaneous values from point to point in the cycle. The lack of perfect balance, which would imply that $E_0=0$ for voltages above and below the resonant voltages for both circuits, is thus indicative of small wave form differences, probably due to the magnetic material. If E is decreased from a high value the characteristic of Fig. 3 may be retraced exactly. The oscillogram*** of Fig. 4 includes the voltage E applied to this circuit and the voltage E_0 of the output. The extreme

*** A continuous record printed in 3 sections for convenience.

voltage selectivity of this bridge circuit is well brought out by this record. The voltage selectivity that is available by this means greatly exceeds in its critical characteristics anything that may be obtained in frequency selective linear circuits. It should be further pointed out that a variable voltage is in general much more economical and simple to obtain than a variable frequency at the same power output.

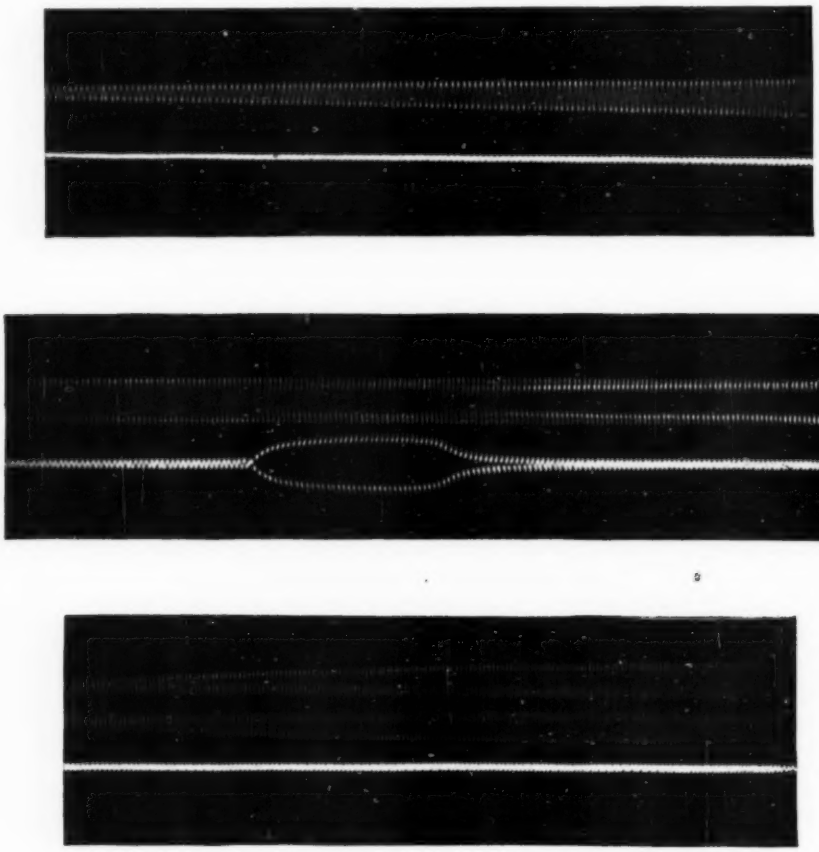

Fig. 4.

Extent of the voltage selective region

Since the resonance voltage for a given core material depends predominantly upon the number of turns on the reactor, this voltage may assume any convenient value within wide limits. Thus the extent of the voltage selective region for a given bridge circuit may be easily determined, and is in fact equal to the difference in the resonance voltages for the two arms of the bridge. In Figs. 5*a*, 5*b*, and 5*c* are shown curves which were obtained by varying reactor turns and hence critical voltage for one arm of the bridge, the other arm being unchanged.

Form of the "resonance peak"

In Fig. 6, curve A, is shown the output voltage E_0 of a typical bridge cir-

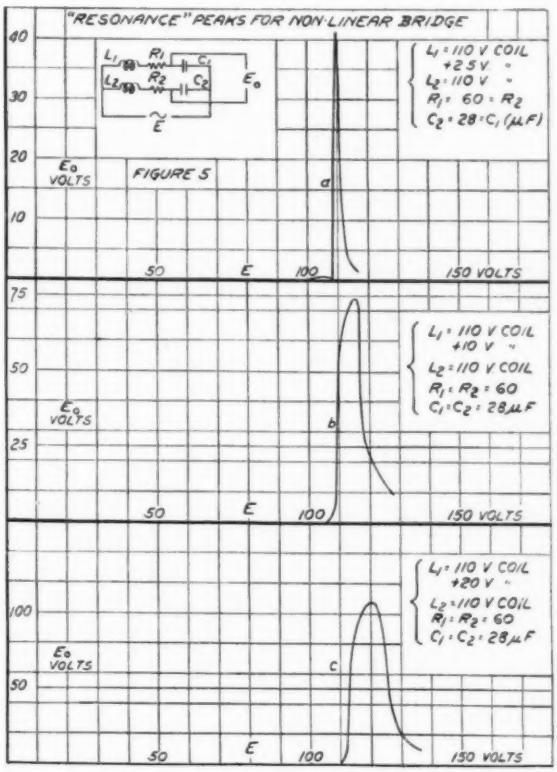
"RESONANCE" PEAKS FOR NON-LINEAR BRIDGE
FIGURE 5
E_0 VOLTS
E
150 VOLTS
a
b
c
L_1 = 110 V COIL +25 V ~
L_2 = 110 V ~
R_1 = 60 = R_2
C_2 = 28 = C_1 (μF)
L_1 = 110 V COIL +10 V ~
L_2 = 110 V COIL
R_1 = R_2 = 60
C_1 = C_2 = 28 μF
L_1 = 110 V COIL +20 V ~
L_2 = 110 V COIL
R_1 = R_2 = 60
C_1 = C_2 = 28 μF

Fig. 5.

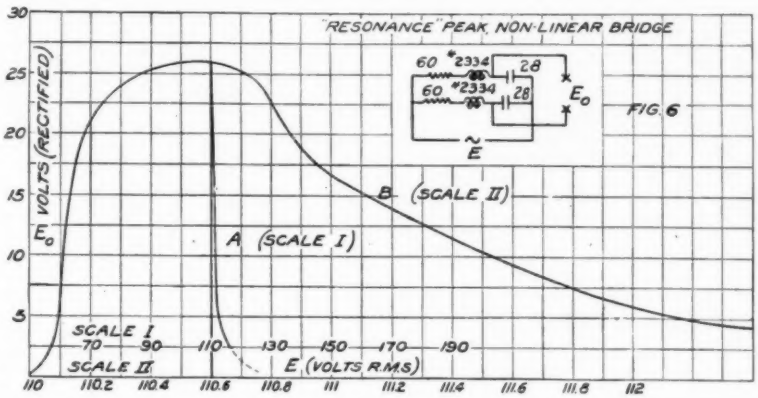

Fig. 6.

cuit as a function of supply voltage E. On the scale to which this curve is plotted it is impossible to determine much about the exact shape of the "resonance peak," and in particular to measure the rapidity with which the volt-

age E_0 varies with the supply voltage E. In order to explore the shape of the $E_0 - E$ curve it is necessary to employ some kind of "suppressed zero" voltmeter since the total portion of the scale which is to be read is confined to a few volts. But the simple series circuit of Fig. 1 has precisely this characteristic, and may be used therefore as a voltmeter. A circuit of this type was in this manner calibrated as a voltmeter so that approximately 80 percent of the current scale was confined to the region 106–114 volts. By the use of this voltmeter circuit the resonance peak of Fig. 6*A* may be explored; this result is given in the same Fig. 6 as curve *B*, which is plotted to scale II. It may be seen that the "peak" is really flat topped and that the initial portion is very steep. At the point of inflexion of the steepest portion it is to be observed that 1/100 percent change in supply voltage E causes the output voltage E_0 to change by approximately 100 percent.

Application to relays

The properties of the nonlinear bridge circuit make possible the construction of voltage selective relays. A simple relay circuit of this type is shown in F . 7*a*.

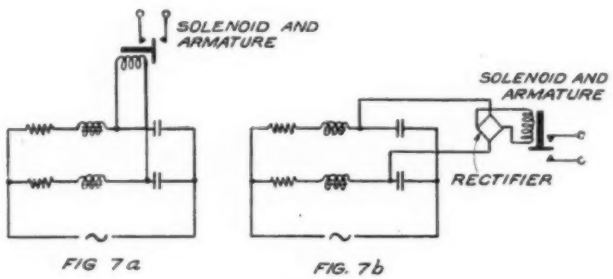

Fig. 7.

In this relay a mechanical contactor is placed at the output terminals of the bridge in such a manner that the armature is attracted only when this output voltage rises. Relays of this construction have been operated in the laboratory. It should be recognized that in general the power utilization of a load supplied by a bridge circuit is not great, and that such relays are therefore comparatively inefficient.

It is found, however, that the substitution of the more efficient d.c. contactor in series with an oxide type rectifier, for the a.c. contactor, is sufficient improvement in power utilization to allow the construction of practical small selective relays requiring only a few watts of power to control many hundred watts in the load circuit. This preferred form of the selective relay is shown in Fig. 7*b*.

Application to industrial and supervisory control problems

The special properties of voltage selective relays make possible the easy solution of many types of control problems which were formerly accomplished with elaborate apparatus, if at all. Classical problems, like the control of mul-

tiple circuit over a two wire system, are among the easier things that can be simply done with this new tool. Methods for providing this and other types of selective control are outlined in subsequent paragraphs.

Many circuits may be controlled selectively if a multiple arm bridge is employed as shown in Fig. 8. Here the bridges a, b, c, $\cdots$ are supplied in parallel by the voltage E, supposed variable. Each bridge controls a load selectively in such a manner that the multiple loads A, B, C, $\cdots$ may be chosen at will by simple variation of voltage at the source. This is shown dia-

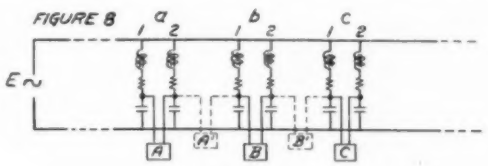

Fig. 8.

gramatically at Fig. 9 where, to a horizontal voltage scale, the characteristics of the bridges a, b, c, $\cdots$ controlling the loads A, B, C, $\cdots$ are drawn. Since it is practical to design bridge circuits for widely varying voltage limits it is clear that a great number of circuits may be selectively operated in this manner.

The limiting number of circuits that may be selectively operated in parallel depends upon the voltage selective region through which each relay operates, the voltage "spacing" of adjacent relays, the constancy of the frequency, and the safe over-current rating of the lowest voltage bridge circuit. Thus when the bridge c is selected, Fig. 8, the current in the arms of bridge a is over 200

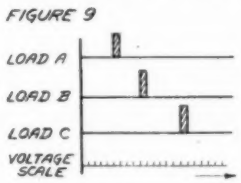

Fig. 9.

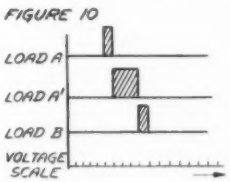

Fig. 10.

percent the value it had at the resonant voltage. Provision must thus be made in the design to provide for this over-voltage condition.

An alternative manner of selectively controlling circuits by means of the nonlinear bridges is available where it is desirable to remove the voltage internal between successive relays. This property may be had for example if load devices are located between *adjacent series circuits* (as indicated by the dotted lines of Fig. 8) instead of between *adjacent pairs* of circuits as shown originally. Thus, in Fig. 10, the control diagram is shown for the loads A, A', B, $\cdots$ of Fig. 8. Load A is deenergized at the same voltage and time for which A' is energized, and so forth, for additional loads. A further modification which will be obvious results from the addition of load devices between *alternate series circuits*, for example, between circuit al and bl of Fig. 8. In this manner different loads may be simultaneously energized in a variety of ways.

Direction-selective relays

If the *family* of volt-ampere characteristics for different values of resistance is obtained for the circuit of Fig. 1, it will be observed that for values of resistance less than a certain critical value the curve for increasing voltage does not coincide with the curve for decreasing voltage. This phenomenon, for which no satisfactory theory is available, is shown in Fig. 11. The value of applied voltage for which the current rises rapidly has been called the "critical voltage for nonlinear resonance" or simply the *resonant voltage*. Similarly, the value of decreasing voltage for which the current suddenly drops to a low value will be referred to as the "critical voltage for dissonance in nonlinear circuits," or simply the *dissonant voltage*. It is to be observed from Fig. 11

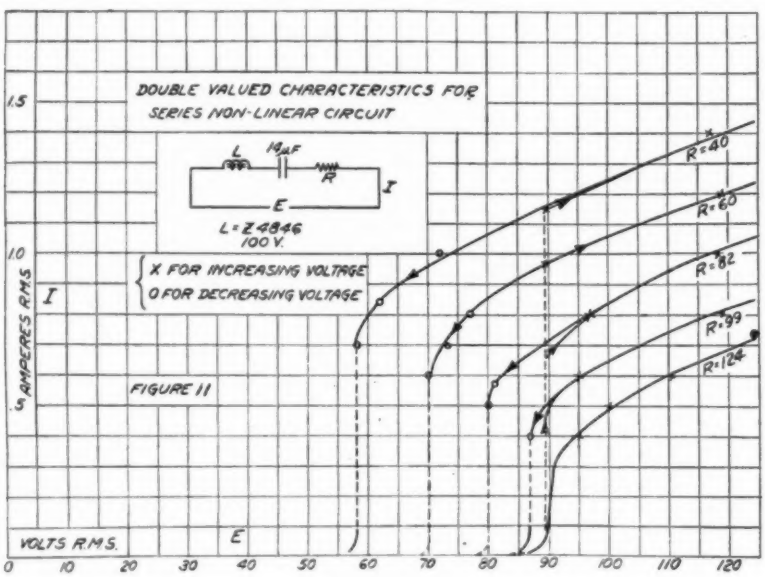

Fig. 11.

that the dissonant voltage is easily determined by variation of resistance in the circuit, and that this may be done without materially changing the resonant voltage. This is an accidental result of great convenience in the design of relay and control circuits; the resonant voltage (or the "pick-up" voltage of a relay) is determined predominantly by inductance, while the dissonant voltage for a given inductance (determining the "drop-away" voltage of a resonant relay) is adjustable by variation of resistance, almost to the exclusion of other factors.

It should be emphasized that in order to obtain the volt-ampere characteristics of Fig. 11, the variation in voltage must be smooth and continuous, such as, for example, that provided by an induction regulator.

Multiple load circuits may be actuated in a different sequence for increasing voltage, than obtains for decreasing voltage by employing this "hysteretic" property of the nonlinear series circuit. For example, in Fig. 12 is

shown a diagram for the bridges a, b, c, $\cdots$ of Fig. 8. Consider the case in which the resonant voltages of the bridge circuits occur in the order a, b, c, $\cdots$ for increasing voltage while the dissonant voltages, had for decreasing voltage, are in opposite order. It is clear that for this case the sequence of selective operation which takes place depends upon the direction of change of voltage, as shown in Fig. 12, where the loads are energized in the order A, B, C, $\cdots$ for increasing voltage, in the order $\cdots$ C, B, A, for decreasing voltage.

By the variety of means described a great number of different control operations may be carried out by means of only two control wires. For some cases this control may be entirely nonmechanical. The advantages of the systems appear to lie in the fact that the component circuit elements are of a simple and economical type, and that a simple actuating means, namely a change in voltage, is economically obtainable. It is believed that these circuits will find their natural application in industrial control and supervisory control problems where an enormous latitude in the selective operation of equipment is provided.

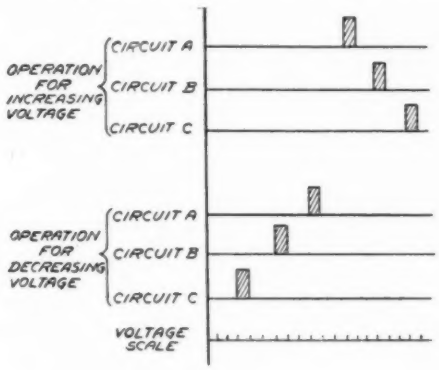

Fig. 12.

Nonlinear bridge as a constant voltage source

It is a curious anomaly that the same bridge circuit which is capable of yielding the extremely critical change in output voltage E_0 with supply voltage E(1/100 percent results in 100 percent E_0) shown by Fig. 6 is also capable of producing under slightly different circuit conditions a constant output voltage E_0 which is to a high degree independent of applied voltage E. The bridge circuits which have been described thus far have been made up of two series nonlinear circuits with approximately equal resistance and capacitance elements, but with inductance elements which differ in the number of turns on the core. Bridge circuits with constant voltage properties comprise identical capacitance and inductance elements, but require dissimilar resistances. For example, the bridge output voltage E_0 as a fuction of supply voltage E is shown in Fig. 13 where curves are given for different values of resistance in one arm; all other elements remain unchanged during the experiment. It may be seen that for applied voltages less than the resonant voltage (which was ap-

proximately the same for both arms) the output voltage E_0 is small for all values of R_2. This output voltage may be thought of as the *difference* in the voltages sustained by the condensers in the separate series circuits; the in-

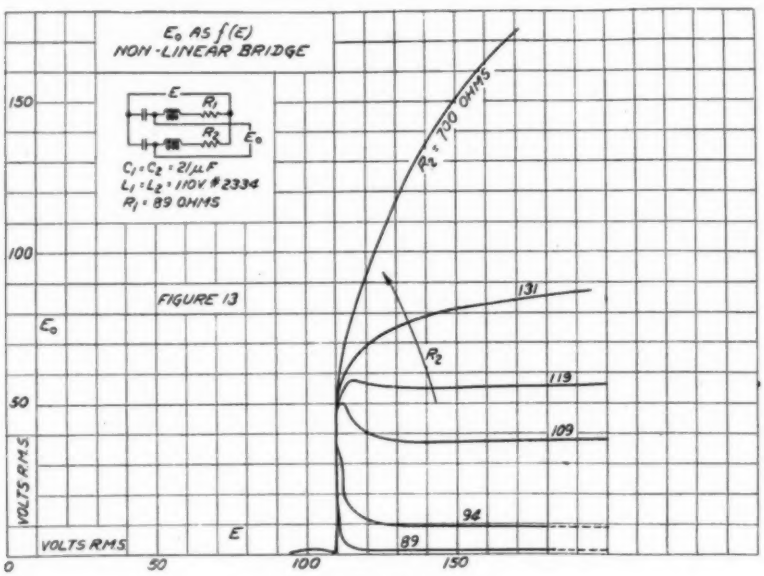

Fig. 13.

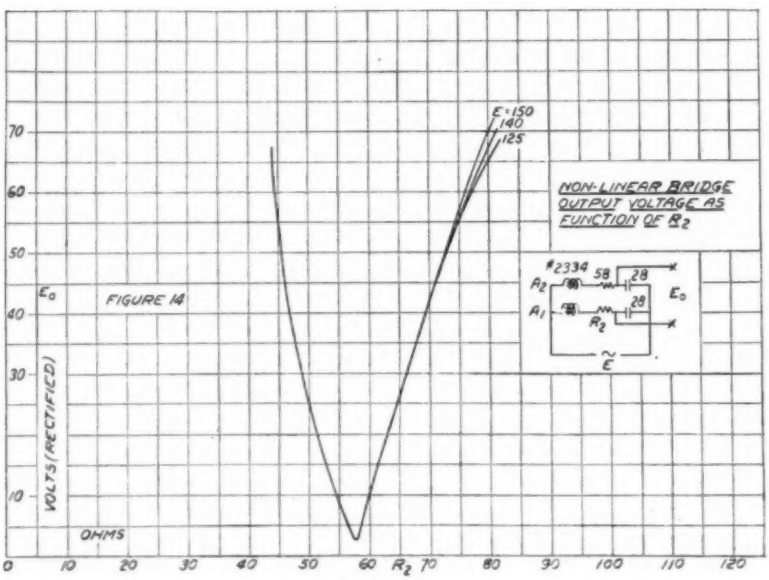

Fig. 14.

stantaneous value of this "difference voltage" is thus determined by the differences in wave shape of the condenser voltages from point to point in the cycle. The curve for $R_2 = 89$ is taken for the case in which the constants of the

two arms are ostensibly identical; the voltage E_0 should therefore be ideally zero.

The curves for successively larger values of R_2 indicate two important points, (a) for values of E greater than the critical voltage, the voltage E_0 tend to become constant, and (b) the voltage E_0 varies rapidly with R_2. If the output E_0 is measured as a function of R_2 for a similar bridge, a curve of the general type of Fig. 14 is obtained. It may be seen that curves for $E = 125$, 140, 150 volts superimpose within the limit of accuracy of the measurement, which is indicated approximately by the width of the line. The variation of E_0 with R_2 is rather striking. In the region $R_2 = 59$ ohms a 2.5 percent change in resistance results in a change in output voltage E_0 of 100 percent.

The predominant property of this nonlinear bridge circuit used in this manner is thus a large independence of supply voltage combined with great sensitivity to resistance.

A further modification of the circuit consists in employing identical inductance and resistance elements but dissimilar capacitances. It is found that for this case (curves not shown) that E_0 depends upon capacitative impedance in approximately the same manner as upon resistance in the bridge previously considered. This circuit is thus critical in capacitance and insensitive to voltage.

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STUDIES WITH AN IONIZATION GAUGE

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(Received June 13, 1931)

Abstract

An ionization gauge of the type described by Found and Dushman was calibrated for helium, neon, nitrogen, argon and mercury. The results obtained have been compared with those derived by means of a graphical integration based on the probability of ionization of different gases as a function of electron velocity. The agreement is very satisfactory. The present results indicate that the purely empirical relation between sensitivity and "molecular number" (total number of electrons per molecule), reported in the earlier paper, is not generally valid.

Experimental Results

THE improvements that have been made in high vacuum technique during recent years have made the subject of very low pressure gauges increasingly important. Among the various measuring devices, the ionization gauge, in some form, has proved to be the most satisfactory tool within the range for which it is designed. Its low pressure limitation is the limit of sensitivity of the current measuring instrument used, and with the development of vacuum tube amplifiers for very small direct currents[1,2] there should now be no serious difficulty in measuring the highest vacua attainable.

The gauge under consideration here is the one described by Dushman and Found[3,4] in two papers in the Physical Review. Quoting from the first paper: the gauge "consists of two tungsten filaments, each wound in the form of a double spiral and mounted coaxially on a four lead stem which is sealed into the lower end of a glass tube about 4 cm in diameter and 12 cm long. The inner spiral is made of 5 turns of 0.125 mm (5mil) tungsten wire wound on a 2.25 mm (89 mil) mandrel. The outer spiral is made of 3 turns of 0.125 mm wire wound on a 3.65 mm (144 mil) mandrel. Surrounding the spirals is a Mo cylinder about 12 mm in diameter and 12 mm long, which is supported on a two lead stem at the upper end of the tube."

This type of gauge has been in almost constant use in this laboratory for nearly ten years. Any three electrode tube may be used as an ionization gauge,[5] but because of its high insulation qualities and the ease of evacuation and outgassing of the metal parts, the Dushman-Found construction, with little or no modification, has maintained its position against all alternative designs. The method of exhaust described in the paper quoted above is the best

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[4] Found and Dushman, Phys. Rev. **23,** 734 (1924).
[5] Found and Reynolds, J.O.S.A. and R.S.I. **13,** 217 (1926).

today, although inductive heating of the cylindrical electrode saves much wear and tear on the filaments. Particular care is needed in bombarding the two sets of filament leads as experience has shown these to be among the most troublesome sources of gas during operation. In use, the inner spiral filament is operated as cathode, the outer spiral as anode at a positive potential, and the cylinder is maintained negative as collector of positive ions.

The uses of the ionization gauge can be separated into two fields. It may be used to measure gas pressures of the order of one barye or greater, depending on the nature of the gas. For this use the gauge is operated drawing 0.5 milliamperes to the anode, which is 125 volts positive, and the collector 22.5 volts negative. For pressures from 0.1 barye downward to the limit of measurement, the gauge is operated with 20 m.a., +250 volts, −22.5 volts. For both operating ranges the efficiency of ionization, expressed in microamperes positive ion current per barye pressure, differs markedly for different gases.

In the 1924 paper, Found and Dushman reported that with a gauge operated at 0.5 ma., +125 volts, −22.5 volts, the efficiency of ionization for several gases and vapors varied directly with the number of electrons in the molecule (referred to subsequently as the "molecular number"). Table I is taken directly from page 737 of that paper. In it $1/K$ is the sensitivity in microamperes/barye and N is the molecular number. The constancy of KN over such a range of values of N is indeed remarkable.

TABLE I.

Gas	$1/K$	N	KN
Helium	0.36	2	5.5
Neon	0.92	10	10.8
Nitrogen	1.51	14	9.4
Carbon monoxide	1.39	14	10.1
Argon	1.72	18	10.6
Mercury	7.6	80	10.5
Iodine	9.8	106	10.5

The object of the present work was the study of this relation between constitution of gas and efficiency of ionization. The investigation was confined principally to gauges of the Dushman-Found type. These tubes were constructed as faithfully as possible after the original specifications. Calibrations were carried out with neon, nitrogen and argon, and, in a few cases with helium and mercury. The gases were the purest obtainable. The nitrogen was prepared by admitting dry air into the system and burning a tungsten filament until the pressure reached a constant value. A McLeod gauge of sensitivity $P = 0.216 \times (\text{cm}^2)$ baryes, especially constructed and calibrated, was used as the standard of pressure. The calibration with mercury vapor was made at the equilibrium pressures for 0°C and 15.5°C.

In Table II are tabulated the results of these calibrations. Gauges 1, 2, 2A were standard except for collecting cylinders 13 mm diameter and 16 mm long. Gauges 27060, 27086, 27107 were of the standard design. Gauge 27545 was

identical with the last three except for having a bottom in the collecting cylinder. The gauges B-1 and B-2 were tested by Mr. J. S. Bacon. The first had a large double spiral of 0.30 mm tungsten wire, 12 mm in diameter for col-

TABLE II. (*0.5 m.a.; +125 volts; −22.5 volts*).

Gauge	Neon	Helium		Nitrogen		Argon		Mercury	
	S	*S*	*R*	*S*	*R*	*S*	*R*	*S*	*R*
1	0.33					2.6	(7.9)	4.5	(13.6)
2	0.28					2.2	(7.9)		
2A				1.4		2.0			
27060	0.25			1.2	(4.8)	1.8	(7.2)		
27086	0.21			0.95	(4.6)	1.7	(8.1)		
27107	0.20	0.15	(0.75)	1.1	(5.5)	1.7	(8.5)		
27545	0.10	0.15	(0.77)	0.86	(4.5)	1.4	(7.4)		
B-1	0.23			1.2	(5.2)				
B-2	0.38			1.9	(5.0)	2.3	(6.0)		
FP 62									
1	0.40	0.23	(0.58)	1.7	(5.0)	2.1	(5.3)		
2	0.43			2.0	(4.6)				

TABLE III.
20 m.a.; +250 volts; −22.5 volts.

Gauge	Neon	Helium		Nitrogen		Argon		Mercury	
	S	*S*	*R*	*S*	*R*	*S*	*R*	*S*	*R*
1	19					80	(4.2)	200	(10.5)
2A				66		88			
27060	18			60	(3.3)	74	(4.1)		
27086	17			50	(2.9)	82	(4.8)		
27107	21	9.8	(0.47)	55	(2.6)	75	(3.6)		
27545	15	9.2	(0.62)	51	(3.5)	70	(4.7)		
B-1	11					34	(3.1)		
B-2	9			19	(2.1)	32	(3.6)		

lector, and the second a mesh cylinder of the same dimension. The two tubes FP-62 were triodes of the familiar UV-200 construction with flat oval plates and hairpin filaments. Under the heading *S* is given the sensitivity in microamperes per barye. Variations in sensitivity are to be expected as a result of geometric differences. However, the ratios of sensitivities for different gases should be expected to be more nearly constant. In Table II, neon is taken as a standard, and the figures in parentheses, *R*, are ratios with *S* for neon taken as unity. Table III presents similar data for the 20 m.a., +250 volts, −22.5 volt range.

The variations of the ratio, *R*, from gauge to gauge, are larger than are desirable. Even for tubes of the same design they are of the same magnitude as the variations in sensitivity, which might indicate a random error in measurements of approximately ±10 percent. Such an uncertainty is unlikely. A later section of this paper presents an analysis of the factors determining the sensitivity for different gases and the effect of slight geometrical differences, due, perhaps, to sagging of filaments on overheating, might conceivably account for part of the observed variability.

Table II shows definitely that the relation between S and molecular number is not a linear one. Comparison with the data of Table I shows very good agreement for the sensitivity for argon, but the values for the others, particularly helium, neon and mercury, cannot be reconciled. Certain it is that the extrapolation of a calibration for one gas to apply to other gases or vapors must be done with caution, if at all, and cannot be accomplished by use of the ratio of molecular numbers. Found and Dushman were aware that the molecular number relation was not a general one for they report, for the 20 m.a.,

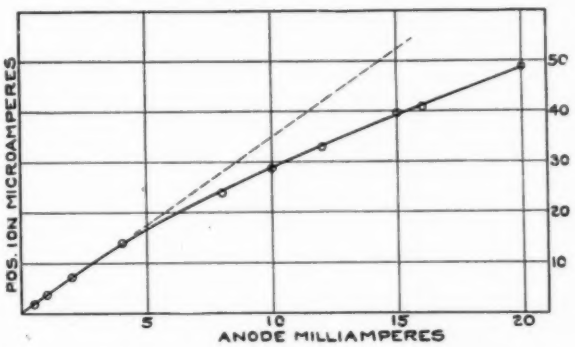

Fig. 1. Variation of sensitivity with anode current. Gauge 1, mercury, 0.24 barye pressure, 250 anode volts.

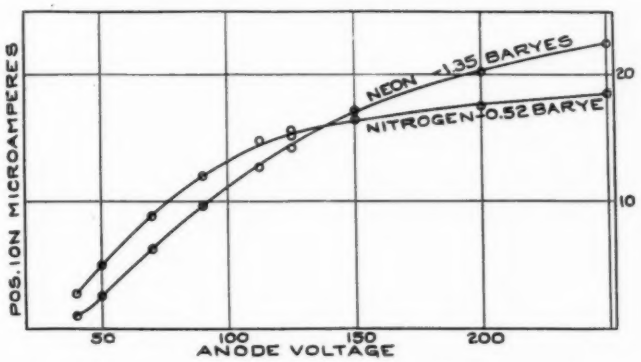

Fig. 2. Variation of sensitivity with anode voltage. Gauge FP 62, 10 m.a. anode current.

+250 volt, −22.5 volt range, sensitivities for argon and mercury of 78 μa/barye and 265 μa/barye. These are in the ratio of 1:3.4 instead of a calculated 1:4.4.

The effects of variation of electron current and anode voltage found check well with earlier published curves. Figs. 1 and 2 show the nature of these relations. The lack of linearity of positive ion current with electron current becomes more pronounced at low pressures, due to the effect of space charge.

Comparison with Probability Ionization

The probability of ionization of different gases as a function of electron velocity has been studied by a large number of investigators[6,7,8,9,10,11,12].

Fig. 3 presents the results on probability of ionization as a function of electron velocity as recorded in the literature. The ordinates are expressed as "the number of ions produced per electron per cm. path at 1.0 mm pressure." Most of the results are given for 0°C, but Compton and Van Voorhis' are for 25°C. These have not been converted to the standard temperature because the ionization gauge results, with which they are to be compared, have not been corrected for temperature variations.

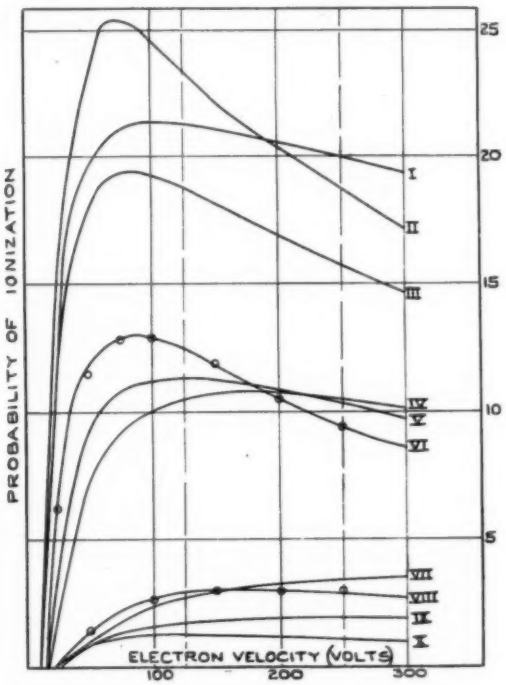

Fig. 3. Probability of ionization as function of electron velocity. Ions per electron per cm path at 1 mm pressure.

The curves are identified as follows: I. Mercury—Compton and Van Voorhis; II. Mercury—Bleakney; III. Mercury—Smith; IV. Nitrogen—

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[11] Bleakney, Phys. Rev. **34,** 157 (1929); Bleakney, Phys. Rev. **35,** 139 (1930); Bleakney, Phys. Rev. **35,** 1180 (1930); Bleakney, Phys. Rev. **36,** 1303 (1930).

[12] Smith, P. T., Phys. Rev. **36,** 1293 (1930); Smith, P. T., Phys. Rev. **37,** 809 (1931).

Compton and Van Voorhis; V. Argon—Compton and Van Voorhis; VI. Argon—Smith; VII. Neon—Compton and Van Voorhis; VIII. Neon—Smith; IX. Helium—Compton and Van Voorhis; X. Helium—Smith. The circles represent results of Bleakney for argon and neon. They coincide almost exactly with Smith's results of VI and VIII.

The method employed by these investigators consisted in shooting a beam of electrons of homogeneous constant velocity into a relatively field free enclosure and collecting the positive ions produced. The electrons, after passing through the ionizing chamber, entered an electron trap, and so traversed the space but once.

These conditions are not realized in the ionization gauge. Here the electron velocity varies continuously. Also all the electrons which are effective

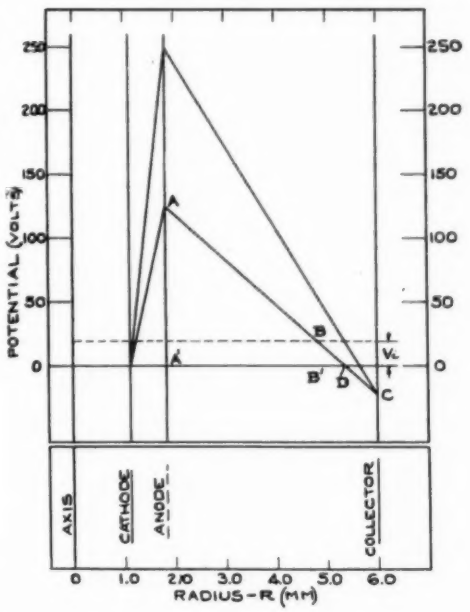

Fig. 4. Potential-geometry relations for the Dushman-Found ionization gauge.

in producing ions cross the space between anode and collector at least twice and most of them do so several times. However, by means of certain approximations, an analysis is possible.

Fig. 4 represents diagrammatically the fields acting upon an electron and the distance an electron travels in the gauge. The electrodes are assumed to be concentric cylinders and the radial fields are assumed linear. Since most of the ions produced in the space between cathode and anode are probably collected at the cathode, this space need not be considered. When the electron passes A' it has acquired a velocity determined by the applied anode voltage, V_a. Between A' and B' the electron has energy enough to produce ionization by collision. V_i is the ionization potential of the gas being studied. At D it is stopped, and returns along the same path. It may be immediately

collected at the anode A', or it may oscillate an indeterminate number of times before finally coming to rest there. The distance travelled in which ionization may occur is, therefore, some multiple of $2A'B'$.

In Fig. 3 it was shown that the probability of ionization by electron collision varied with the electron velocity. The probability of an electron producing an ion in one journey across the space $A'B'$ can be determined by integrating under the *probability of ionization* curve (Fig. 3) between the limits of the ionizing potential and the maximum accelerating voltage V_a, and multiplying the result by the distance $A'B'$ in centimeters. This probability multiplied by I_e, the electron current emitted by the filament, gives I_p' the positive ion current produced at 1 mm pressure in a gauge operated with I_e milliamperes and V_a volts, assuming that an electron traverses the ionizing space $A'B'$ but once.

These operations were carried out for all the curves of Fig. 3. The areas under the curves were obtained with a planimeter. I_p' was calculated for the 0.5 m.a., 125 volt and the 20 m.a., 250 volt calibrating ranges. The results, reduced to 1 barye pressure and expressed in microamperes of positive ion current, are given in Table IV. In Table V, the calculated values of I_p' for each gas have been averaged, each determination receiving the same weight, and the averages listed in the second column. In the third column is the average sensitivity of the gauge experimentally determined. In column IV, α is the multiplication factor needed to bring the calculated and experimental values into agreement. Lastly, in column V, $I_p = \alpha I_p'$ and the agreement between S and I_p in columns III and V is seen to be as good as that between two gauges of identical construction.

I_p' was derived on the basis of the electrons making one crossing between A' and B'. Obviously two or more trips must be made. Mr. B. J. Thompson, formerly of this company, has calculated the average number of times an electron traverses the space between the grid and plate of a triode tube before being collected. The equation used is $Z = (2\theta/1-\theta^2)I_e$ where Z is the average number of trips made by the electron, θ is the effective open area of the grid, and I_e is the electron current emitted by the filament. An experiment with gauge 27107 in good vacuum showed that with grid and plate at the same accelerating potential, approximately 85 percent of the electrons passed through the grid to be collected at the plate. Using this information, $\theta = 0.85$, and $Z = 6.4\ I_e$. Thus, according to this reasoning, I_p' should have been multiplied by 6.4 in order to obtain the calculated sensitivity I_p. We have seen that for best agreement, the factor α was 3.9. Putting this figure 3.9, for Z and working backward, we find that the value $\theta = 0.80$. makes the two constants α and Z identical. This value for θ is a perfectly possible one and allows us to attribute the multiplied constant α to the effect of successive excursions of electrons across the ionizing space.

It is not, however, necessary to assume this lower value to θ to bring I_p' and S into agreement. The calculations were made on the assumption of a linear field between anode and collector (Fig. 4). Actually, the field between the two electrodes must approximate a logarithmic curve, concave upward,

TABLE IV.

	Sensitivity in amp. $\times 10^{-6}$ per barye pressure	
	0.5 m.a., 125 volts	20 m.a., 250 volts
Helium		
Calc. C. & V.V. (IX)	0.037	2.9
Calc. Smith (X)	0.030	2.0
Observed	0.15	9.8
Neon		
Calc. C. & V.V. (VII)	0.055	4.7
Calc. Smith-Bleakney (VIII)	0.065	4.7
Observed	0.22	19
Nitrogen		
Calc. C. & V.V. (IV)	0.27	18
Observed	1.1	55
Argon		
Calc. C. & V.V. (V)	0.34	20
Calc. Smith & Bleakney (VI)	0.42	22
Observed	1.7	77
Mercury		
Calc. C. & V.V. (I)	0.75	40
Calc. Smith (III)	0.65	33
Calc. Bleakney (II)	0.80	42
Observed	3.0	180

TABLE V.

I	II	III	IV	V
Gas	I_p' Average	S Observed	$\alpha = \frac{S}{I_p'}$	I_p Calculated
	0.5 m.a.; +125 volts; −22.5 volts			
He	0.033	0.15	4.6	0.13
Ne	0.060	0.22	3.7	0.23
N_2	0.27	1.1	4.1	1.1
A	0.60	1.7	2.9	2.3
Hg	0.75	3.0	4.0	2.9
			Average = 3.9	
	20 m.a.; +250 volts; −22.5 volts			
He	2.5	9.8	3.9	9.7
Ne	4.7	19	4.1	18
N_2	18.	55	3.1	70
A	21.	77	3.7	82
Hg	39.	180	4.6	150
			Average = 3.9	

and in a direction to shorten the distance $A'B'$. Also all electrons were assumed to pass the anode with velocities determined by the applied voltage V_a. There is, of course, a velocity distribution with V_a representing the maximum. The open spacing of the anode coil makes the number of electrons entering the space $A'B'$ with velocities less than V_a relatively large, another factor tending to decrease the average ionizing path $A'B'$.

Any corrections which could be made for these two disturbing effects would be at best only roughly approximate. They do, however, operate in a

direction to decrease the calculated sensitivity I_p and bring it in closer agreement with the experimental observations. Thus, starting with the structural dimensions of the ionization gauge, the published values of probability of ionization and fairly tenable assumptions as to potential distribution, it is possible to predict the sensitivity of the gauge for five gases with almost the accuracy of the experimental determinations.

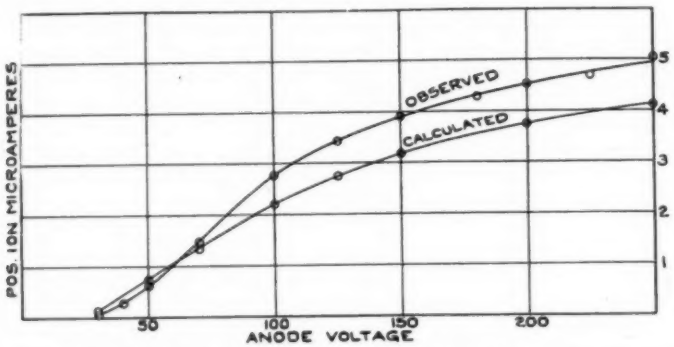

Fig. 5. Sensitivity as a function of anode voltage. Gauge 27086, argon 2.1 baryes, 0.5 m.a. anode current. Comparison of observed and calculated curves.

A further assurance of the reasonableness of these calculations is shown in Fig. 5. Here is plotted the observed variation of sensitivity with anode voltage for gauge 27086 with argon at 0.25 barye pressure. On the same plot is the curve calculated from the data of Compton and Van Voorhis (Fig. 3-V). Here again the agreement is nearly as close as between two tubes of the same construction.

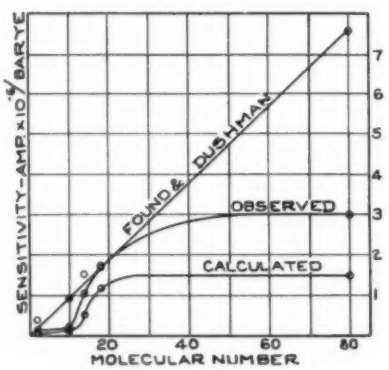

Fig. 6. Comparison of different gases. Gauge operated at 0.5 m.a., +125 volts, −22.5 volts.

Finally, Fig. 6 compares the efficiency of ionization of the ionization gauge, for the five gases studied as determined in this research, as calculated from probability ionization data and as reported by Found and Dushman. It will be at once apparent that there is a radical difference between the two experimental curves. For argon, the present calibration of the gauge agrees with that obtained by Found and Dushman.

For the other gases there is a discrepancy between the two sets of observations, and in the present investigation it has been found impossible to reproduce the results obtained earlier. While a perusal of the original records fails to show any plausible reason for such a discrepancy, it is probable that some unknown variation in experimental conditions led to the particular relation between molecular number and ionization efficiency which must now be regarded as a pure coincidence.

It was the question of the validity of this relation which led Dr. S. Dushman to suggest the present investigation. The author takes pleasure in acknowledging his indebtedness both to Dr. Dushman and Mr. C. G. Found, to Dr. L. Tonks for valuable criticism and to Mr. B. J. Thompson and Mr. J. S. Bacon for contributions indicated above.

AN ELECTROMAGNETICALLY CONTROLLED THREE-ELECTRODE VACUUM TUBE

By F. B. Haynes
Virginia Polytechnic Institute

(Received June 26, 1931)

Abstract

A three-electrode tube in which the electron current is controlled by means of a magnetic field instead of the customary electrostatic field. This is accomplished by means of a special type of "grid", the construction of which determines the static characteristic of the tube.

THE common type of three-electrode tube makes use of an electrostatic control of the electron flow from filament to plate. This electron flow or plate current may also be controlled by a magnetic field with the aid of a properly constructed third electrode or grid.

Construction. The filament of this tube consists, preferably, of a single filament *F* (Fig. 1) which is located along the axis of the tube. *G* of the same

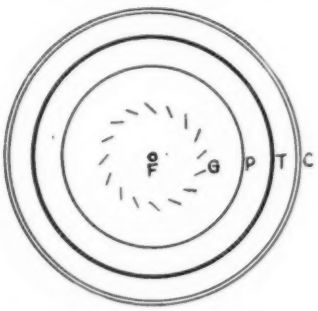

Fig. 1. Cross section of tube. *G* shows construction of grid.

figure shows the construction of the grid which consists essentially of a series of metal strips placed parallel to and cylindrically around the filament. These strips are oriented at about an angle of 45° with respect to the periphery of the circle on which they are placed.

For low frequencies the grid may be readily constructed by cutting parallel slits in a small sheet of metal and bending one edge of each strip outward so that it has the appearance of the lower part of the hood of an automobile. This sheet is then bent into the form of a cylinder and placed around the filament.

P of Fig. 1 is the plate and *T* the tube which is evacuated. The control coil *C* is placed around the tube in such a way that the resulting magnetic field is along the axis of the tube.

Theory of operation. The filament is heated and the plate given a positive potential, the grid being connected directly to the filament or is given a bias

as may be desired. If, now, the control coil is connected to a source of d.c., the resulting magnetic field will cause the electrons moving from the filament to the plate to be deflected either in a clockwise or counter-clockwise direction (Fig. 1), depending upon the direction of the field. If the deflection is in a counterclockwise direction, the plate current will be reduced as a result of more of the electrons striking the grid. If the deflection is in a clockwise direction, the plate current will be increased, due to the construction of the

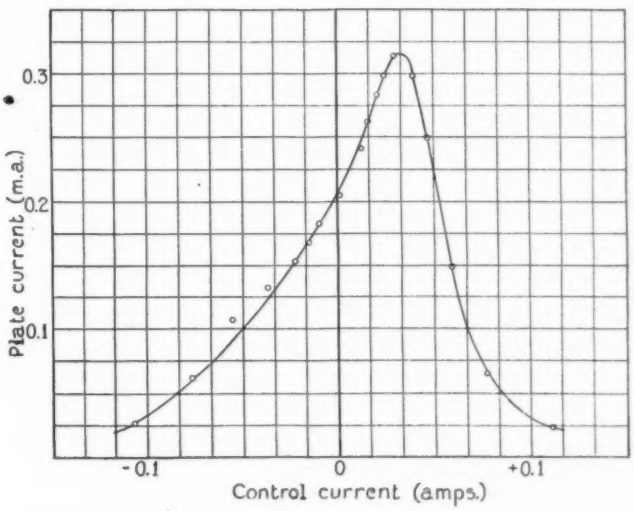

Fig. 2. Static characteristic of tube.

grid, for a small field or control current but will be decreased again if the control current is increased.

These characteristics are brought out in the experimental curve shown in Fig. 2. Control current (+) means that the current in the control coil is in one direction and control current (−) means the control current is in the reverse direction. A change in spacing and orientation of grid strips will obviously alter somewhat the form of the curve.

By use of a proper "magnetic bias" the tube may be made to operate on any part of its characteristic curve.

RELATION OF LONG LINE CURRENTS TO SOIL CORROSION

By Stanely Gill and W. F. Rogers*
Gulf Oil Companies, Research Department, Houston, Texas

(Received June 24, 1931)

Abstract

"Stray currents" from street electric railways and the like give rise to rapid corrosion of buried pipe lines. A type of currents similar to "stray currents," but which occur at long distances from any possible external source of electric current, has been found on pipe lines. These currents are known as "long line currents" and are supposed to originate between the soil and the pipe. They frequently follow the pipe for miles without any change in amperage. To determine possible influence of these currents upon corrosion, measurements of their value were made on an 8-inch oil line upon which much corrosion trouble had been experienced. The line was removed from the ground and the extent of corrosion determined by inspection. Electrical resistivities of numerous samples of soil were determined.

From the data obtained, the following conclusions are drawn:

1. Discharge or accumulation of electric currents of the class which have been termed "long line currents" is, in general, without influence upon corrosion of buried pipe lines.

2. Electrical resistivity of soil correlates to a certain extent with corrosion of buried pipe; the relationship is not sufficiently consistent to be of practical value.

3. There is no consistent relationship between soil resistivity and the accumulation or discharge of "long line currents."

Introduction

RECOGNITION of the fact that buried pipe-lines carry direct electric currents which are not attributable to leakage from utility systems is due to the work of Mr. K. H. Logan of the Bureau of Standards.[1] Mr. Logan termed these currents, which persist over considerable distances, "long line currents." They are distinguished from stray currents by being a function of the line itself, being derived independently of extraneous influences. It is believed that these currents are primarily due to electrolytic action between the pipe line and the soil. Galvanic circuits of all dimensions, from those obtained between adjacent spots on the pipe surface to those extending over several miles, are believed to exist on buried pipe lines. As an arbitrary definition, all of these galvanic circuits which give rise to currents persisting over any appreciable length of pipe may be classed as "long line currents."[2]

[1] Logan, Rogers and Putnam, "Pipe Line Currents," Trans. of A.P.I. Meeting, Section IV, p. 116, (1930).

[2] A more detailed discussion of the several classes of current affecting pipe lines will be found in the paper cited above and also in a paper by Gill and Rogers, "Electric Currents Carried in Lines," Oil and Gas Journal **29**, T158 (1930); see also Shepard, U. S. Bureau of Standards Journal of Research **6**, 683 (1931).

These "long line currents" could be of practical significance to the operator of a pipe-line system only if they were found to bear a definite relationship to the corrosion of the buried pipe. The studies of these phenomena which the writers have conducted upon lines of the Gulf Pipe Line Company have dealt, to a certain extent, with the factors which give rise to "long line currents", but have been more directly concerned with a determination of the practical value of current measurements in the prediction, detection and mitigation of pipe-line corrosion.

The detailed survey described in this paper was undertaken as a step in this program. An 8-mile pipe-line, in territory known to be highly corrosive, was to be raised and reconditioned. Before the reconditioning operations were started, and while the line was in regular operation, measurements of electric current were made over its entire length, and thus serve to locate accurately all points at which the line either picked up or discharged current. When the line was raised and cleaned, it was thoroughly examined; the deepest pits on each joint of pipe were measured. The electrical conductivities of samples of soil taken from the side of the pipe at intervals of 100 feet over the entire length of the line were determined. Numerous additional samples of soil were taken to the laboratory for more detailed examination.

The pipe-line investigated was laid in 1922, of 8-inch; 29 pound per foot, screwed and coupled, open-hearth steel pipe. Located in Jefferson County, Texas, it connects the Lucas and Elvista stations of the Gulf Pipe Line Company; the former station is located on the southern edge of the Spindletop oil-field, while the latter is 4 miles north of the Port Arthur refinery of the Gulf Refining Company. When laid, this pipe was coated with a coal-tar cut-back paint; at the time of the inspection, this paint had disappeared completely.

Methods Used in Making Survey

Electrical Contacts

Contact for the electrical measurements was made by the use of $\frac{1}{4}$ inch steel drills, which were mounted in the ends of pieces of $\frac{1}{2}$ inch pipe and forced against the pipe surface with a pressure of about 150 pounds by the use of weights and levers.[3] The drills were rotated until the electrical readings showed that they had penetrated all scale, and had made contact with clean steel.

Fig. 1 shows this assembly set up in the field. A tripod mount holds the $\frac{1}{2}$ inch pipe in a vertical position. To the lower end of this pipe is attached a $\frac{1}{4}$ inch steel drill, the point of which is immediately at the top center of the pipe. The horizontal pipe is staked to the ground at one end and has a 25 pound weight hung on the other end. The ratio of the lever arms causes a 75–150 pound force to bear upon the drill, pressing it into the pipe.

Measuring Instruments

Difference in potential between the points of contact thus made was meas-

[3] Rogers (Discussion); Trans. of A.P.I. Meeting, Part IV, p. 122 (1930); Stanley Gill and W. F. Rogers; "Electric Currents Carried in Lines," Oil and Gas Journal **29,** T158 (1930).

ured by the use of a special Leeds and Northrup service potentiometer. This instrument has two scales: full-scale readings are, respectively, 5 millivolts and 16 millivolts. On the 5 millivolt scale, readings are accurate to ± 0.01 millivolts.

Method of making measurements

The procedure followed in making measurements is as follows: Contact to the line was made at points *A*, *B*, and *C*. (Fig. 1) Measurements of changes in potential from *A* to *B* and from *B* to *C* were made. Contact *A* was then moved to *D*, 100 feet ahead of contact *C*, and changes in potential from *B* to *C* and from *C* to *D* measured. Wherever an unusually large change of potential took place, intermediate contacts were used to locate the point of accumulation or discharge within 25 feet.

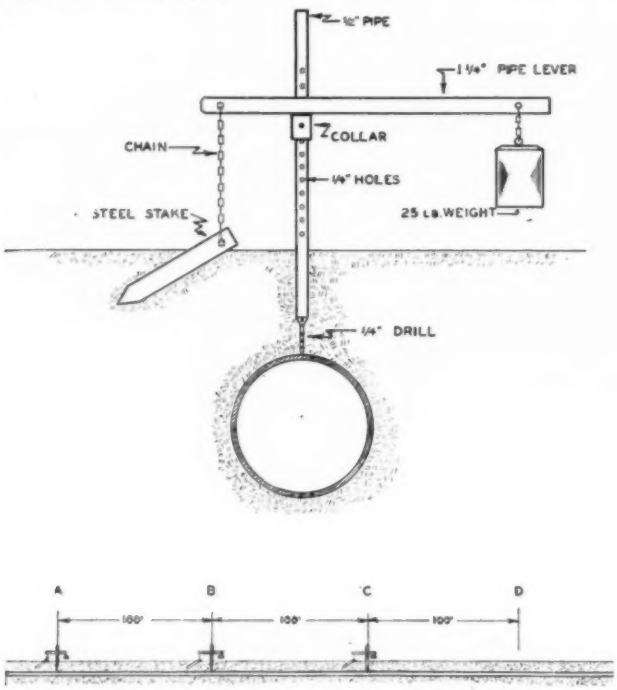

Fig. 1. Electrical contact for buried pipe lines.

Fig. 2 shows the *B* contact set up on the pipe, the potentiometer, and the switch which connects it across contacts *A* and *B* or contacts *B* and *C* (Fig. 1).

Calculation of current

The magnitude of the electrical current carried by the line is computed directly from the potential gradient. In the case of 8 inch, 29 pound line pipe, a potential change of 0.72 millivolts per 100 feet indicates a current of 1 ampere. The calculated currents will be in error to an uncertain degree, because of variations in the wall thickness of the pipe; this error is inevitable in any method of current measurement which is based upon determination of potential gradients.

Change of current

From the standpoint of corrosion correlations, the change of electrical current carried by the line is of basic importance. If there exists correlation between corrosion and these currents, corrosion would occur on those sections of the line which were discharging current to the soil, and would be inhibited on those portions of the line which were accumulating current from the soil; the corrosion would be independent of the actual flow of current in the pipe stself, depending only upon flow of current between pipe and soil. As a means of studying this correlation, rates of change of current on each 100-foot section of the line were calculated. Where measurements were made on sections which were less than 100 feet in length, rates of change were calculated in units of amperes per 100 feet. In expressing these data, a positive

Fig. 2. Electrical contact and potentiometer set up in field.

sign is used to express accumulation of current, and a negative sign to express discharge of current from the line.

Measurement of soil resistivity

At 100-foot intervals, over the entire length of the line, samples of the soil at the level of the pipe were taken for determination of their electrical resistivities.

These soils were taken to the laboratory, saturated with specially prepared distilled water, and compacted into a conductivity cell; resistivities were measured by the use of a 60-cycle alternating current, Leeds and Northrup ohmmeter (wheatstone bridge). The cell used is made up of hard rubber, with silver electrodes; the cell constant has been determined by the use of accurately standardized potassium chloride solutions, and is checked periodically.

It is not necessary to exercise extreme care in the use of exactly the proper

quantity of water for saturation of the soil samples; numerous measurements have shown that the resistivity, as measured in this cell, is not greatly affected by slight differences in moisture content, provided the soils are approximately saturated with water.

This method of measuring resistivities of soils in the laboratory, while they are saturated with water, has been found more useful than any field method. The reason for this lies in the fact that the resistivity of a soil, as measured in the field, is determined by a random moisture content, while the laboratory measurements are made under standard conditions, and are truly characteristic of the soils. The resistivity of a soil, as determined by this method, corresponds closely to that which the soil will possess in place, when saturated with water; when not so saturated, the resistivity will be somewhat higher, depending upon the degree of saturation.

Measurement of pipe corrosion

The pipe was carefully examined immediately upon being raised from the ditch, and, again, after having been thoroughly cleaned. The general type of corrosion was described, and the depth of pits on top, bottom and sides of the pipe determined. Visual estimation of depths of pitting was checked by frequent measurements of pit depths; a depth micrometer was used for this purpose.

Additional observations

Other observations, made as a part of the survey, included the following:

(a) A topographic map serves to locate features which would be expected to influence corrosion, and also to record the data in such form that subsequent tests can be accurately controlled.

(b) Surface levels, and pipe elevations, form an important part of this topographic survey.

(c) Location of old leaks, either in the line under examination or in parallel lines, was recorded.

(d) The character of the soil was determined by visual examination; classification of the soils was also determined from the U. S. Bureau of Soils Soil Survey of Jefferson County.[4]

(e) Numerous samples of soil were taken to the laboratory for thorough physical and chemical examination; these samples cover all portions of the line where unusually severe or unusually mild corrosion has been experienced.

Summary and Discussion of Electrical Data

General

The country traversed by this line is a part of the Texas Coastal Plain; surface elevations fall from about 20 feet above sea level, at Lucas, to about 7 feet above sea level, at Elvista. Most of the land is pasture, though there is some cultivation. Natural vegetation is confined to grass and low shrubs.

[4] "Soil Survey of Jefferson County, Texas," United States Dept. of Agriculture, Bureau of Soils (1915).

Flow of current over approximately half of the 8-mile section is toward Lucas Station, where are located 90 large steel storage tanks. Over this section the line is, on the average, accumulating current. There are, of course, many points of discharge set up by more or less local action. At a distance of 4 miles from Lucas Station, a reversal of the direction of current flow takes place; over the balance of the line, there are numerous reversals.

It is practically impossible to determine the precision of the current measurements. As a rough, working criterion, it may be assumed that the current measurements are uncertain by at least ± 0.05 ampere, and probably by as much as ± 0.1 ampere. The chief factor of uncertainty is variation in the thickness of the pipe wall.

Corrosion is rather generally distributed over the entire length of the line. The extent of this corrosion, as determined by the joint-by-joint inspection, is shown in Table I.

TABLE I. *Depth of corrosion pits entire line.*

Depth of deepest pit in joint*	Number of joints	% of total
1/32″ or less	549	27.1
1/16″	642	43.4
1/8″	227	15.3
3/16″	33	2.2
1/4″	13	1.7
5/16″	5	0.3
Average depth of deepest pits—0.071″		

* The term "joint" is used, in pipe-line parlance, to describe a single length of pipe; on the average, each "joint" is from 20 to 23 feet in length.

As in all oil pipe-lines, a considerable part of the serious corrosion is to be attributed to the presence of oil in the soil. A list of depths of pitting in joints of pipe adjacent to collars which had developed leaks during the life of the line shows the accelerating influence of oil upon corrosion:

TABLE II. *Depths of pitting of pipe adjacent to repaired collars.*

Depth of deepest pit in joint	Number of joints	% of total
1/32″ or less	25	14.4
1/16″	60	34.5
1/8″	51	29.3
3/16″	27	15.5
1/4″	11	6.3
Average depth of deepest pits—0.164″		

It is striking that the average depth of the deepest pits on joints of pipe adjacent to these old leaks is more than twice the average for the entire line.

Corrosion and Change of Current

Careful analysis of the data covering the changes of current carried by the line, as compared with the corrosion experienced, leads inevitably to the conclusion that there is absolutely no consistent relationship between these two factors. The data are plotted in Fig. 3. An examination of this plot shows

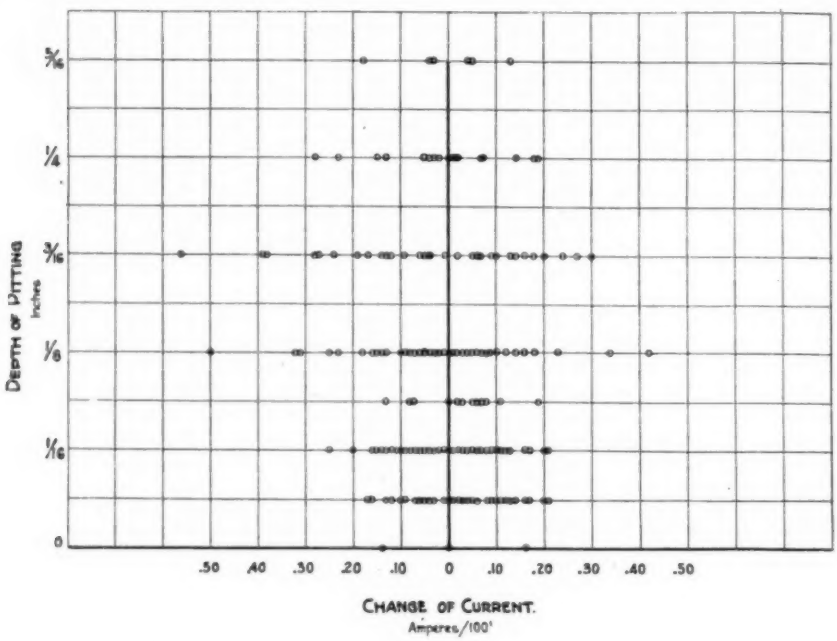

Fig. 3. Relation of pitting depth to change in magnitude of electric current carried by a pipe line.

random distribution of rates of current change at all pitting depths. The complete lack of correlation between change in current and corrosion experience is also shown in Table III.

Table III. *Corrosion and change of current. (By 100-foot sections.)*

Depth of deepest pit in section	Number of sections	Average change of current
1/32″ or less	73	+0.038 amp./100 ft.
1/16″	171	+0.041 amp./100 ft.
1/8″	100	−0.010 amp./100 ft.
3/16″	41	−0.048 amp./100 ft.
1/4″	21	−0.041 amp./100 ft.
5/16″	6	+0.055 amp./100 ft.
Average change of current for entire line +0.006 amp./100 ft.		

Not only is there no relationship between corrosion and the direction of current change, but all of the averages are within the experimental error of ± 0.05 amp.

This is entirely in line with theoretical considerations. The rates of current discharge are so low that the corrosion penetration will be negligible, provided discharge is uniform over the surface of the pipe. Assuming 100 percent current efficiency of corrosion, and neglecting all polarization effects, a uniform and continuous discharge of 1 ampere over 100 feet of 8-inch pipe would result in a corrosion penetration of only 0.002 inches per year.[5] Actually, current efficiencies at such low current densities are extremely low, and a discharge of this magnitude could, theoretically, take place without any corrosion of the metal. Thus, the only possibility of accelerated corrosion lies in a concentration of discharge. It is possible that a concentration of current discharge sufficient to cause corrosion may be present in isolated instances, but it is apparent that this is of negligible importance as a factor in the corrosion of buried pipe-lines.

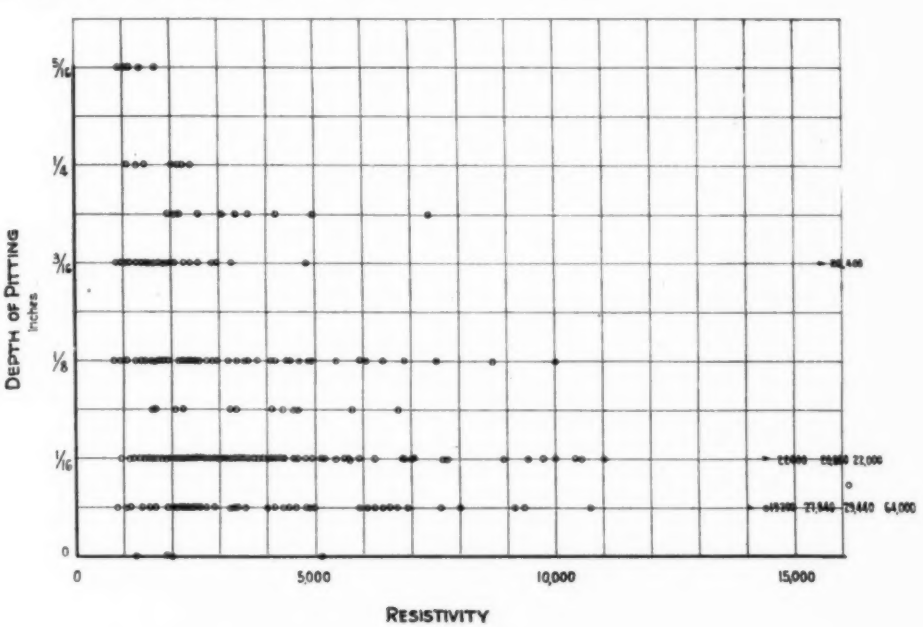

Fig. 4. Relation of pitting depth to soil resistivity.

A second theoretical factor enters into the relationship between corrosion and these electric currents. Careful investigation indicates that the chief cause of the electric currents observed is electrolytic action arising from inhomogeneities of the soil. Assuming a combination of soil characteristics which would cause a given section of a pipe-line to be markedly anodic to adjoining sections of line, and assuming concentration of current discharge from this section, corrosion could occur. As the corrosion proceeded, prod-

[5] The highest rate of discharge which has been observed by the writers in their study of "long line currents" is approximately 1 amp. per 100 feet. In the numerous but somewhat sketchy studies by Shepard (reference 1, page 694) the "most abrupt discharge of current observed throughout the investigation" was 1 amp. in approximately 300 feet.

ucts of corrosion would be deposited on the corroded line. Products of corrosion of iron are cathodic to uncorroded iron; thus, the electrolytic action of the corrosion products would reverse the current discharge responsible for the corrosion, and the section of line in question would tend to accumulate current.

It is obvious, from the brief summary of results presented above, that the accumulation or discharge of currents is without influence upon corrosion of the line in question. These data, in conjunction with results of similar, though

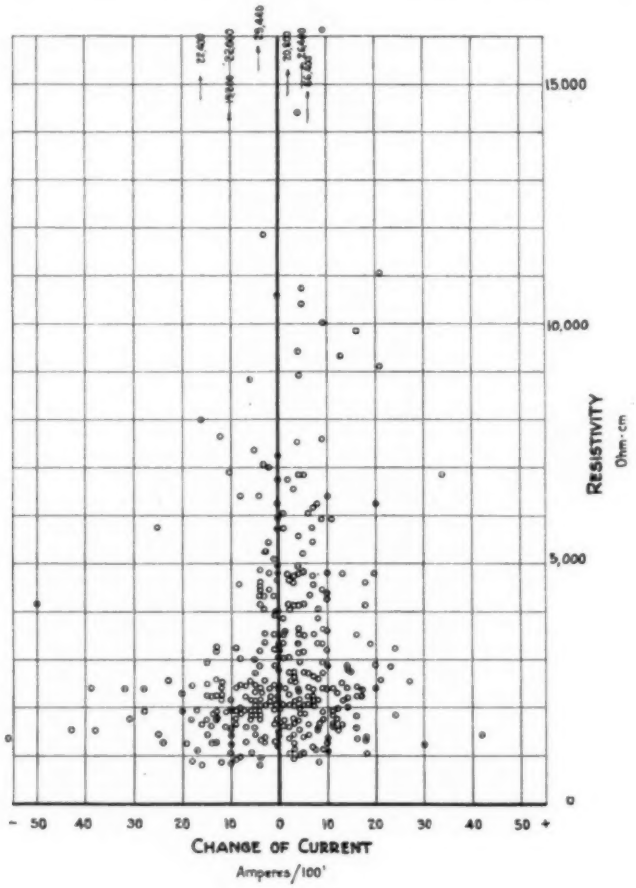

Fig. 5. Relation of soil resistivity to change in magnitude of electric current carried by a pipe line.

less thorough, tests on other lines, lead to the conclusion that the phenomena which may be classed as "long line currents" are without practical significance in relation to corrosion of pipe-lines.

Corrosion and resistivity

Data on the relationship between corrosion of the pipe and resistivity of the soil are plotted in Fig. 4. Although it is not apparent from the distribution of points on this plot, there does exist a slight correlation between these fac-

tors. This relationship is shown in Table IV. Average resistivities are less for the more corrosive soils than for the less corrosive. The figures for maximum and minimum resistivities corresponding to the several corrosion rates are

TABLE IV. *Corrosion and soil resistivity. (100-foot sections.)*

Depth of deepest pit in section	Number of sections	Soil resistivity—Ohm · cm		
		Average	Maximum	Minimum
1/32″ or less	73	5395	64000	1040
1/16″	171	3506	22400	960
1/8″	100	2933	11840	800
3/16″	41	2544	26400	880
1/4″	21	2519	7360	900
5/16″	6	1093	1680	1040

of particular interest; they indicate that corrosion may or may not occur in soils of low resistivity, depending upon other conditions, and that rapid corrosion is not experienced in soils of extremely high resistivity.

Like many other factors, electrical resistivity of soil is undoubtedly concerned in the reactions of soil corrosion. It is not, however, the controlling factor in all cases. Thus, measurements of soil resistivity cannot be expected to correlate with corrosion of buried pipe at all perfectly; they are of value only as a rough index of corrosion tendencies.

Change of current and soil resistivity

Results of the survey, as concerns correlation between change of current and resistivity of soils, are plotted in Figure 5. The fact that there is no consistent relationship is apparent from the plot. A tabular summary of these data, Table V, reveals a slight correlation. Although there can be no certainty, due to the small number of sections experiencing large changes of cur-

TABLE V. *Change of current and soil resistivity. (100-foot sections.)*

Change of current amp./100 ft.	Number of sections	Soil resistivity—Ohm · cm		
		Average	Maximum	Minimum
+0.41 to +0.60	1	1,440	—	—
+0.36 to +0.40	0	—	—	—
+0.31 to +0.35	1	6,880	—	—
+0.26 to +0.30	2	1,900	2,560	1,240
+0.21 to +0.25	6	5,116	11,820	1,840
+0.16 to +0.20	21	3,993	22,400	1,080
+0.11 to +0.15	23	2,757	9,360	1,120
+0.06 to +0.10	61	3,413	16,160	896
0 to +0.05	97	4,061	26,400	960
0	37	3,384	10,560	1,200
0 to −0.05	64	3,600	29,440	900
−0.06 to −0.10	38	3,550	19,200	920
−0.11 to −0.15	27	2,253	7,680	1,280
−0.16 to −0.20	11	2,900	10,000	800
−0.21 to −0.25	5	2,608	5,760	1,280
−0.26 to −0.30	2	2,160	2,400	1,920
−0.31 to −0.35	2	2,080	2,400	1,760
−0.36 to −0.40	2	1,965	2,400	1,530
−0.41 to −0.60	3	2,313	4,160	1,520

rent, these data appear to indicate a slightly greater tendency to the discharge of current in soils of low resistivity. This is particularly apparent in the maxima for each group, although the same tendency is to be noted in the averages. The relationship is not sufficiently consistent to be of any value.

Summary and Conclusions

As a result of a complete electrical and corrosion survey of a typical pipeline in the Texas Gulf Coast, it has been concluded that the so-called "long line currents" possess no practical value in relation to corrosion of the pipe. In detail, the following conclusions were reached:

A. Accumulation or discharge of "long line currents" is without practical bearing upon the problem of pipe line corrosion.

B. Although it is theoretically possible that the discharge of such currents, if concentrated to small portions of the pipe surface, may, sometimes, cause corrosion, this action is of negligible importance in comparison to other causes of pipe corrosion.

C. There is a slight correlation between corrosion and the resistivity of soils. This has but little practical significance; the only valuable conclusion is that serious corrosion is not to be expected in soils of extremely high resistivity. The reverse is not at all true; soils of low resistivity are not, necessarily, corrosive.

D. There is no definite or consistent relationship between soil resistivity and the accumulation or discharge of "long line currents." A slight tendency toward accumulation of current in soils of high resistivity and toward discharge in soils of low resistivity is evidenced by the data, but this is not sufficiently definite to be conclusive.

Acknowledgment

The authors wish to acknowledge the aid of Mr. Cecil McLain of the Research Department of the Gulf Oil Companies in obtaining the data upon which this paper is based. Mr. McLain, as supervisor, made all of the measurements obtained in the field, kept the field notes and prepared the summary tables.

THE EDITOR'S COLUMN

The System of "Atomic" Nuclei

EVER since the discovery of radioactivity and its explanation in terms of the spontaneous disintegration of the atom, there has been a persistent attempt by numerous physicists and chemists to delve more deeply into the mystery of that tiny entity, the nucleus. In the course of time a wide variety of methods for attacking the problem have been developed, one of which was mentioned in this column last month; i.e. hyperfine structure measurements. More familiar studies are those on the radioactive series made by Madame Curie, Lord Rutherford, and many others, and also the detailed studies made of the isotopes of the elements, particularly those due to Aston. The chemists and astrophysicists have also contributed greatly to the solution of the problem by making extensive measurements on the relative abundance of the various atomic species in the earth's crust, in the meteorites which fall on the earth from the outer regions of space, in the sun, and in the stars.

Two phases of this work are considered in papers appearing in current issues of the Physical Review.[1,2] Professor Harkins, who has long been interested in the classification and interpretation of the data, has reexamined at length the material on the types and abundance of the atomic species. He classifies all atoms by means of four parameters; P and N, the numbers of protons and of electrons respectively in the nucleus, Z, the number of atomic electrons outside the nucleus (the ordinary atomic number), and finally n, the "isotopic" number. These quantities, which are all integers, are not all independent but are connected by the relations

$$Z=P-N;\ n=N-Z.$$

By studying the distribution of the various atomic species as a function of these parameters many interesting relations have been found, which are condensed into a set of fourteen rules. While all of the rules are somewhat qualitative, some are very well obeyed. Thus it is very generally true that N is an even number, for out of 156 known atomic species whose atomic numbers are in the range 1 to 60 inclusive, N is even for 125 of them, being odd for only 31. This becomes even more striking when expressed in terms of the relative abundance of the atoms. According to a table given in Harkins' paper N is even for about 98% of the atoms in the earth's crust. This is indeed a percentage! Similarly most atoms have an even value for P, although the figures are not so startling for this case, these atoms making up about 87% of the earth's crust. These two rules are especially important because of their indication of a "pairing" of the electrons, and also of the protons. This tendency of electrons to form "wedded couples" has long been a standard notion in chemical theory, but it is only recently that the quantum mechanics has found a way of including it into the mathematical theory, at the same time allowing the protons also to share the benefits of "matrimony."

Another rule, to which considerable interest is attached, states that for an exceptionally large number of atoms, P is a multiple of 4. This leads to the idea that the α-particle, rather than just the proton, may be a prominent unit in the building up of atoms, since the α-particle (He nucleus) is a very stable structure containing four protons. While this rule is somewhat less quantitative than the others, the five most abundant kinds of atom found in the meteorites are of this type.

While these general facts have been known for some time, others discussed in the paper are new. One of the most interesting points which comes out is the prediction of the existence of new and as yet undiscovered isotopes. Classifying all atoms into four possible series according as P, $P-1$, $P-2$, or $P-3$ is divisible by 4, diagrams are given for

[1] W. D. Harkins, Phys. Rev. October 1, 1931.

[2] H. C. Urey and C. A. Bradley, Phys. Rev. 38, 718 (1931).

each series, plotting the isotopic number n against the atomic number Z. This gives a set of diagrams consisting of a regular and very symmetrical set of points, except that certain points on the diagram are not occupied because the corresponding atoms have not yet been discovered. Supposing that the diagrams should be complete, one can then predict the existence of these atoms. While it is altogether possible that atoms might exist which would not be predicted in this fashion, yet it is of great interest that definite predictions can be made.[3] For details of the argument as well as for the many other relations discussed, reference should be made to the original paper.

UREY and Bradley have investigated one aspect of the question which arises concerning the reason for the large differences in the abundances of the isotopes. To illustrate the problem, let us consider one of the cases discussed by the authors, which is given by the following reaction

$$C^{12}+O^{17}\rightarrow C^{13}+O^{16}. \qquad (1)$$

This indicates that the isotope of mass number 12 of carbon and that of mass number 17 of oxygen interact with each other and give as resultant products a carbon and an oxygen atom of mass numbers 13 and 16 respectively. If we enclose definite amounts of these reacting substances in an isolated space at some definite temperature T_0, then when equilibrium has been established, the concentration of each of the components can be calculated from thermodynamic theory. The relative concentrations will, of course, depend on the temperature T_0. Conversely, if the equilibrium concentrations are known, then the equilibrium temperature can be calculated. Taking the known values for the concentrations of the isotopes in (1), as they are found on the earth at the present time, one can thus calculate the temperature at which the mixture would be in equilibrium with these relative concentrations. That this need not be the present temperature of the earth is evidenced by the radioactive elements which are not now in thermodynamic equilibrium, but it might reasonably be expected that the equilibrium temperature would be around 10^7 degrees (absolute scale) if it is supposed that the material forming the earth were in equilibrium at the time the earth was separated from the sun. The authors have made this formal calculation of the equilibrium temperature for fifteen reactions of the type (1), and find that there is no agreement between the various temperatures so found; some of which even come out negative. Since this calculation is very sensitive to errors in the determination of the atomic weights, the authors have also calculated, by a slight modification in the method, what the mass differences between a number of isotopes, such as, for example B^{11} and B^{10} should be if the equilibrium temperature is assumed to be about 10^9 degrees. These results also are in disagreement with the experimentally determined values. Consequently it appears that, considering all of the isotopes, there is no temperature at which they could be in thermodynamic equilibrium with their present concentrations. This may simply mean that one cannot neglect the part played by radiation in determining the equilibrium state, or there may be still other unknown factors which become important at high temperatures.

[3] Aston has just reported (Nature, Aug. 8, 1931) the discovery of four new isotopes, Sr^{87}, Ba^{137}, Ba^{136}, Ba^{135}. A check of the diagrams given by Harkins indicates a definite prediction of only one of these; viz., Ba^{136}.

Reflection of Electrons in Quantum Mechanics

ONE might be tempted, if one were very bold, to make an experimental test of the predictions of the quantum mechanics in the following (idealized) way. Set up a parallel plate condenser with very large plates, and bore two co-axial holes directly through the plates. Paying no attention to the disturbing effects of these holes on the distribution of the field between the plates, shoot a beam of electrons through the holes in the direction of the field (so that,being negatively charged, they would be retarded by it). According to the classical theory no electrons would pass through the condenser as long as the energy, E, of the electrons was less than the potential difference $(V_+ - V_-)$

$=V$ between the plates, and all would get through just as soon as E became greater than V. Using quantum mechanical theory no electrons would again get through for $E \leqq V$, but for $E > V$ it would still not be true that *all* electrons could pass both holes. A calculation by Wetzel[4] shows, however, that the effect is so small as to be incapable of measurement. Thus for a condensor width of 1 cm and a potential difference $V = 10$ volts, about 98.5% of the electrons would get through for a primary electron energy $E = 10.00003$ volts, and practically 100% would get through for $E = 10.0002$ volts!

[4] W. Wetzel, Phys. Rev. **38,** 1205 (1931).

The Vectorial Photoelectric Effect

IF ONE shines light of sufficiently high frequency ν on the surface of a metal, electrons are liberated, giving rise to the usual photoelectric current. The velocities of these electrons are determined by quantum interchanges of energy between the light beam and the electrons, governed by Einstein's photoelectric equation. As regards the *numbers* of electrons which are liberated, the behavior is quite classical since the magnitude of the photoelectric current is proportional to the intensity of the incident light. There is, however, a still more intimate connection with the classical wave theory in that the current depends on the state of polarization of the incident light. The study of this connection is the object of a paper[5] by H. E. Ives on the vectorial photoelectric effect in thin films of alkali metals. If one plots the photoelectric current from alkali metal surfaces (e.g. platinum which has been coated with a thin film of potassium) as a function of the angle of incidence for plane-polarized incident light in which the electric vector E is in the plane of incidence ($E||$) and also that for which E is perpendicular to the plane of incidence ($E\perp$) the curves show two striking differences; (1) the current for $E||$ is much larger than that for $E\perp$, and (2) there is a pronounced maximum in the curve for $E||$ at around 70° for the angle of incidence. In order to find an explanation for these experimental results, Ives investigates theoretically the ideal problem of a plane metal surface covered with a monatomic film of an alkali metal, since experiments indicate that only the top layer of atoms is effective in producing photoelectrons. Assuming that the number of photoelectrons liberated in any region of the film is proportional to the average intensity of the light in that region, Ives calculates the average intensity of the light at the surface of the metal, using the known optical constants of the *metal*. In this calculation the presence of the film is neglected, it being assumed that the light intensity throughout the film is the same as it would be at the surface of the metal in the absence of the film. The wave pattern at the surface of the metal is, of course, a superposition of the fields due to the incident, the reflected, and the "transmitted" beams, according to the well-known principles of the electromagnetic theory of light. It is interesting to observe, with Ives, that if the metal were a perfect conductor, this procedure would give zero intensity for the light in the film, since the surface of the metal would be a nodal surface for the electromagnetic field; due to the finite conductivity of the metal the interference is not perfect. This effect should be the more noticeable the higher the frequency of the light since the ordinary theory of metallic reflection breaks down for light in the ultraviolet region of the spectrum.

Making a correction also for the size of the irradiated portion of the surface, which varies as the secant of the angle of incidence; Ives finds that this calculation gives a variation of the current as a function of the angle of incidence of just the observed kind, except that the ratio of the currents for $E||$ and $E\perp$ does not come out quite right. The reason for this discrepancy is traced to the neglect of the properties of the film. The correction is made in a purely heuristic manner by supposing that although the film plays no part in determining the wave pattern at the surface of the metal, it does partially play the rôle of an optical barrier in that in order to obtain the force components *within the film* one must apply to it the boundary conditions of the electromagnetic theory, calculating the

[5] H. E. Ives, Phys. Rev. Sept. 15, 1931.

dielectric constant from the optical constants of the material composing the *film*. That a monatomic film should at all approximate the material in bulk as regards its optical properties is very interesting since one would suppose a thickness comparable to the wavelength of the light, that is, three or four thousand atoms deep, would be required. The theory gives quite good results for films of alkali metals deposited on metals, but does not work so well for films deposited on glass, for some reason which is not apparent.

Light Quanta and Electrodynamics

THE modern hypothesis of light quanta occupies a very peculiar position in current physics. In the study of light, *per se*, such as is contemplated in physical optics, it has no place for the wave theory masters the situation beautifully. Historically it was developed in the attempt to explain the facts of the interaction of light with matter. Einstein's interpretation of the photoelectric effect by means of the light quantum is well known, while the discovery of the Compton effect gave the photon a just claim to being classed as an observable entity, at least in so far as circumstantial evidence can be accepted as proving existence. But still it remained outside the current of the unified electromagnetic theory of radiation and matter. The main characteristics of the photon are expressed in Einstein's two relations connecting its energy with its frequency and with its linear momentum respectively; i.e. $E=h\nu$ and $E/c=P$. These two relations are ample to give a reasonable theory of the Compton effect. But in addition to this it is known that when an atom absorbs or emits radiation it can change its angular momentum, hence if these dynamical properties are to be conserved during the process, there must be some property of the photon corresponding to an angular momentum, which in turn must be connected with what is called the polarization of the light in the wave theory. A photon thus becomes a rather complicated dynamical system.

A definite, and quite successful, attempt was made by Dirac[6] to develop a real quantum mechanical theory of photons, on a par with the theory of atoms. For this purpose he employed an old device used many years ago by J. H. Jeans and also by Lorentz, which consists in enclosing the radiation in a "box" having perfectly reflecting walls. It is a familiar fact that in such an enclosure only light of certain frequencies can exist; i.e. only standing waves, quite like the standing waves which occur on electrical lines, or as exhibited mechanically on a violin string. Reflection at the boundary sets up a destructive interference for waves which do not have the proper frequency. This is the wave picture of the radiation. If one proposes to describe it in terms of light quanta, then it is possible to correlate the light quanta with the standing wave system in a definite and unique way; i.e. each standing wave of frequency ν represents a set of photons of energy $E=h\nu$. Of course it is just this possibility of passing from waves to quanta which lends point to the whole scheme. Having made this correlation one can proceed to develop the theory of the interaction of light quanta and the matter which may be present in the cavity by using the classical laws of electromagnetic theory for the interaction of the radiation with the matter. That is, one calculates the interaction of the radiation and the matter just as though the former were electromagnetic waves, and then interprets the result in terms of light quanta. It is to be noted, however, that there can be no question of a corpuscular theory of light in the same sense as for electrons since a photon does not maintain its identity during an absorption or emission process. One can only deal with the number of photons of each type present in the radiation field at a given instant.

Heisenberg and Pauli[7] have attempted to go back a step further in order to develop a field theory which could replace the old electromagnetic theory and yet which would give results of a "quantum" type as well as be in accordance with relativity theory. The comparison of this theory with that of Dirac is

[6] P. A. M. Dirac, Proc. Roy. Soc. **A114,** 243 and 710 (1927); I. Waller, Zeits. f. Physik **61,** 837 (1930).

[7] W. Heisenberg and W. Pauli, Zeits. f. Physik **56,** 1 (1929); **59,** 168 (1930).

the subject of a recent paper by Oppenheimer.[8] In attempting to build up a theory of photons and to bring it in line with a field theory, one has as a guide the "wave-mechanical" theory of the atom, especially in its relativistic form due to Dirac, in which corpuscular electrons are described by means of a continuum of waves. One is also guided by the known selection rules for linear and angular momenta for the interaction of matter and radiation which are valid to a high degree of accuracy, as is evidenced by the vast amount of work which has been done in unravelling the spectra of the atoms. For example, suppose an atom in a magnetic field emits a photon travelling along the direction of the field. Then the component of angular momentum of the atom in the direction of the field changes by one Bohr unit. Thus the photon must also have a component of angular momentum of one Bohr unit in its direction of flight, the sign of the component depending on the state of polarization of the photon.

Passing over the arguments, for details of which reference must be made to Oppenheimer's paper, we shall simply look at some of his conclusions. Since one is trying to get a corpuscular theory of light quanta paralleling that for electrons, it might be expected that the two theories would show quite analogous results. Oppenheimer finds this to be so with somewhat disastrous results. The theory predicts the existence of photons with negative energies, just as Dirac's relativistic equation for the electron predicts the existence of electrons in negative energy states. It is possible to avoid this difficulty, but only at the expense of creating others. Thus the simple light quantum theory predicts that at the zero-point of temperature, all of the light quanta crowd into the state with zero frequency so that the energy in the field vanishes. The field theory, on the other hand, shows an infinite residual zero-point energy. Thus the hypothesis of light quanta leads to quite formidable difficulties in the building up of a consistent quantum electrodynamics. Of course these difficulties are intimately related to the analogous difficulties in the relativistic theory of the electron, and the whole complex of problems will probably have to be solved more or less at the same time.

E. L. HILL

[8] J. Oppenheimer, Phys. Rev. **38**, 725 (1931).